

A STUDY IN THE OXIDATION OF KRAFT BLACK LIQUOR

By
PETER MAURO RICCA

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This dissertation was undertaken as a fundamental research project at the University of Florida Air Pollution Laboratory. Black liquor oxidation, a process which reduces odors and other air-borne chemical losses, has seen limited use in the Kraft paper industry. Technical difficulties caused by unique characteristics of southern black liquor have impeded the employment of this process in the southeastern United States. In this research an attempt was made to provide some general process design criteria which are applicable regardless of location or liquor characteristics. The relative importance of temperature, oxidant pressure, method of contact, and type of gaseous oxidizing agent was determined. The chemical reactions that occurred during oxidation were also investigated.

A southern Kraft black liquor containing 6.1 grams per liter of sodium sulfide was oxidized using pure oxygen. This alkaline sodium base black liquor also contained polysulfide, thiosulfate, sulfate, carbonate, hydroxide, and soluble organic matter. A non-foaming bench scale contactor was used and certain physical and chemical parameters varied. The predominant inorganic reactions that occurred were the oxidation of sodium hydrosulfide to sodium polysulfide and sodium thiosulfate. The thiosulfate reaction was slightly reversible

although the polysulfide reaction was not. The mole ratio of polysulfide to thiosulfate formed by complete oxidation of the hydrosulfide was relatively independent of temperature. Approximately 1.0 moles of sodium polysulfide was formed for every 1.6 moles of sodium thiosulfate produced. Oxidation below 60°C precipitated small quantities of amorphous sulfur droplets from the liquor. These droplets upon aging crystallized to rhombic sulfur which in turn decomposed and re-dissolved in the alkaline black liquor.

The method of gas-liquid contact affected the rate of reaction but not the quality nor quantity of the major inorganic reaction products. Oxidation at 60°C required the least volume of oxygen, but oxidation proceeded most rapidly at 75°C. Therefore the optimum oxidation temperature lay between 60°C and 75°C. When adequate gas-liquid contact was made available, the reaction rate was limited by the oxidation rate of hydrosulfide. This oxidation very closely approximated a first-order reaction.

Evidence collected suggested that the organic material present in the black liquor catalyzed the oxidation of the hydrosulfide. Oxidation took place in two distinct steps: first, absorption of oxygen and, second, the utilization of this oxygen to oxidize the hydrosulfide. Undesirable side reactions that also utilize some of the absorbed oxygen were increasingly prevalent above 60°C.

Pure oxygen at atmospheric pressures had only limited effectiveness in oxidizing the odorous constituents of black liquor. Oxidation fixed the inorganic hydrosulfide but at least a portion of the

organics still remained volatile. These materials were subject to loss when the black liquor was recycled to reclaim the unused chemicals. Thus it was necessary to further treat the oxidation exhaust gases to completely eliminate odors. These residual odors were identified and effective means to destroy them with ozone were investigated. Approximate costs and suggestions for mill-scale application of pure oxygen and ozone were discussed.

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CHAPTER I

INTRODUCTION

Atmospheric Pollution and the Pulp and Paper Industry

Only in recent years have the expansion of industrial activity and concentration of population created severe and widespread problems known as atmospheric pollution. The Manufacturing Chemists Association¹ defines atmospheric pollution as "the presence in the air of substances put there by the acts of man, in concentrations sufficient to interfere with the comfort, safety, or health of man, or with the full use and enjoyment of his property." Therefore, in order to have atmospheric pollution problems, three conditions must exist simultaneously: there must be a source of pollutants; a susceptible population or other receptor; and a mechanism for transport between the two.²

"The source may be any activity of man or nature which releases to the atmosphere any dust, fume, gas, mist, odor, smoke, or vapor. The population or receptor can be people, vegetation, domestic animals, homes or manufacturing plants. Susceptibility of the population is measured in terms of health, economics, aesthetics, and toxicity. For a problem to exist, source and susceptible population must be brought together by the common bond of transport which is controlled by topography and meteorology."²

Numerous sources of pollution may be active in any given locality. Industrial operations, steam-electric generating plants, food processing

operations, incinerators, and automobiles are some of the major contributors of air-borne material to the environment. Since atmospheric pollution cannot be legislated out of existence, control activities must be governed by sound economic, nuisance, and health factors.

Pulp and paper manufacturing is the fifth largest³ manufacturing industry in the United States. Except in areas where low cost water and rail transportation are available, pulp mills are frequently situated near their sources of raw materials. The vast forests of the southern Appalachian mountains and the gulf coast states have prompted industrial growth in the wood and wood-products field. Today the southeastern United States is one of the greatest pulp and paper producing areas of the world.

Associated with pulp and paper making are various problems of waste treatment and environmental change. Over the past few years the Air Pollution Research Laboratory at the University of Florida has studied the polluttional aspects of the air-borne emissions from the sulfate paper industry. During this time methods have been developed to identify and monitor these effluents.^{4, 44}

The most prevalent complaint concerning the sulfate pulp and paper industry is the emission of odorous gases into the atmosphere. Under stable meteorological conditions the typical "rotten cabbage" Kraft mill odor can be detected tens of miles from a plant site. The odorous gases commonly emitted from the Kraft process result mainly from the recovery of black liquor. These gases contain sulfur in the form of hydrogen sulfide, sulfur dioxide, alkyl mercaptans, and their oxidation products.

Commercial devices are available for controlling gaseous emissions. However, the emission of odor-producing materials, because of the many points of release and the low concentrations involved, is not amenable to reduction by conventional control devices. The heart of the problem may be found at the point where these materials are initially formed rather than where they are emitted into the atmosphere. It is often easier to improve a process by preventing the evolution of an elusive material than to try to collect the material after it is formed. This study concerns the fundamental chemistry of black liquor oxidation -- a process which may be used to reduce the quantities of odorous gases lost from the chemical recovery system of the sulfate process.

Kraft Process

The Kraft pulping process was introduced in Germany in 1879 as an improvement over the soda method. It was discovered that if wood chips are cooked in a liquor containing a mixture of sodium hydroxide and sodium sulfide instead of plain sodium hydroxide (caustic soda), the resulting pulp could be made into a high strength paper sheet. Hence, the German word Kraft, meaning strength, was the name given to the new process. This process is interchangeably known as the sulfate process because the chemical make-up is added to the process in the form of sodium sulfate or salt cake.⁵

In Kraft pulping the wood is barked, chipped, and placed into large pressure digesters along with the solution of cooking chemicals. The chips are cooked at about 115 pounds pressure (344°F) for one to

six hours. Following the digestion period, the material is dumped into a blowpit or blowtank where the liquor containing the noncellulosic portions of the wood is drained from the pulp. During digestion the sulfide in the cooking liquor combines with organic and inorganic materials to form noxious gases which are released into the air when the digester is opened.

The pulp is washed with hot water to remove the remaining chemicals. The drainage from the blowpit and pulp washers is known as black liquor and is stored hot in insulated tanks. The pulp is screened, refined, thickened, sometimes bleached, and then converted into paper.

In the chemical recovery cycle the black liquor is concentrated in multiple-effect and direct-contact evaporators, then burned, and the heat used to produce steam. During evaporation and handling volatile sulfur compounds continue to be lost. Evaporator exhaust contains gases similar to those released in the digester blow tank. Effluent gases from the recovery furnace contain both sulfurous gases and particulate matter.

The ash or smelt from the recovery boiler contains the inorganic chemicals, but in a chemically reduced form, that were present in the black liquor. This smelt is dissolved in water to produce a green liquor containing sodium sulfide and sodium carbonate. During solution some gases are produced and these are vented into the atmosphere. The green liquor is causticized by the addition of slaked lime and clarified to produce white liquor which is returned to the digesters to process more wood. A flow diagram of the Kraft process is shown in Figure 1.

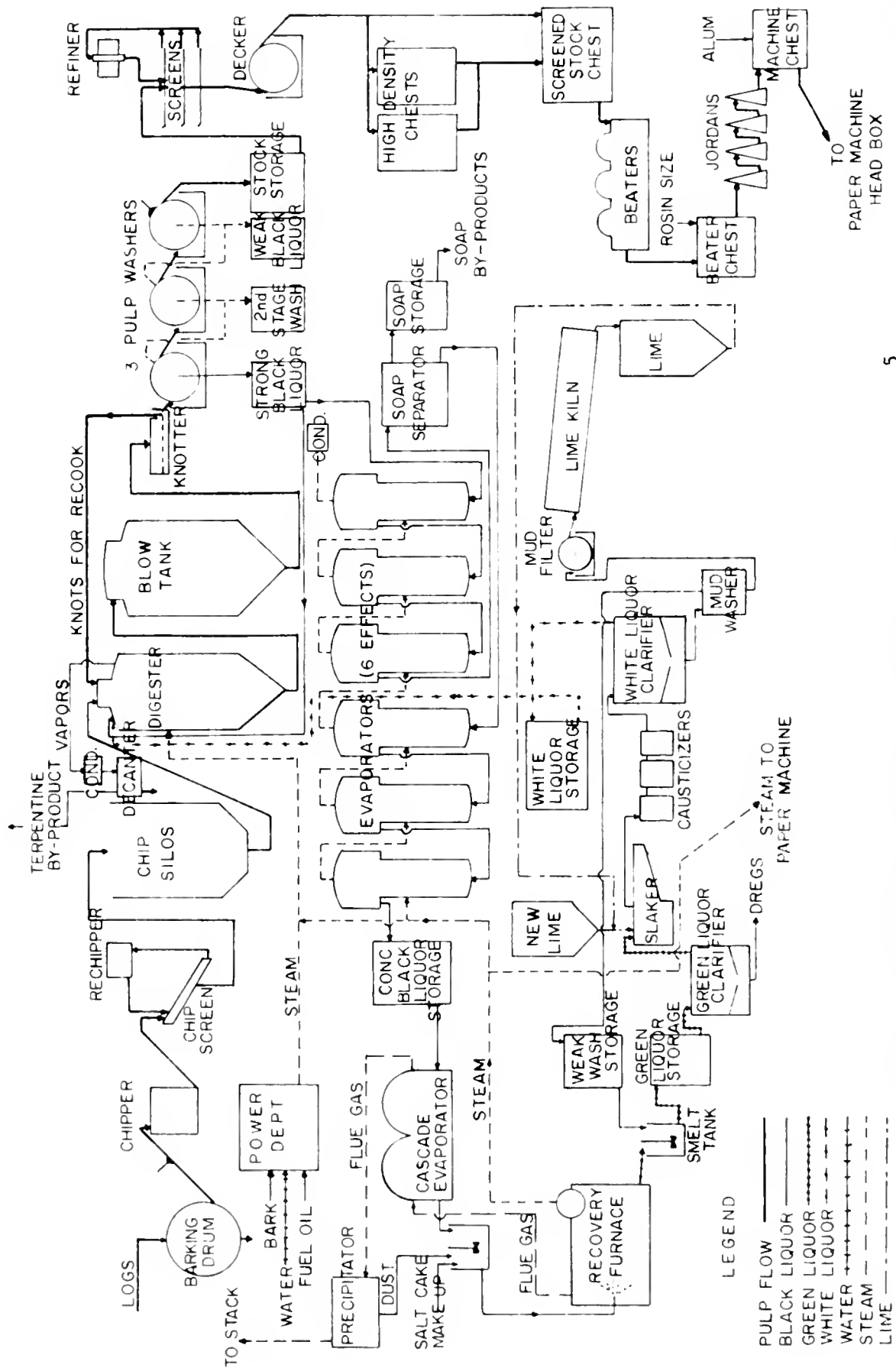


Fig. 1.— The Kraft (Sulfate) process for pulp production.

Kraft paper making has expanded greatly in the past 20 years. This growth has been prompted by the economy of the process and the ever increasing uses for its high-strength pulp. Presently more than 75 per cent of the paper-grade pulp produced in the United States is made by the Kraft process.

Pollution Control and Black Liquor Oxidation

Building and operating a completely odorless Kraft mill is possible but expensive because a small amount of material must be eliminated from a large amount of hot gas. For a Kraft mill to be completely odorless all sources of emission must be controlled, maintenance and operation must be excellent, and equipment must not be overloaded. However, when sulfate mills are not located in densely populated areas, 100 per cent control is neither necessary nor economical.

The sources of air-borne gaseous and particulate emissions from a Kraft mill are tabulated in Table 1.

Chemical losses from the recovery boiler can be reduced by installation of cyclones and electrostatic precipitators or wet-type scrubbers. In some instances all three devices are used. Evaporator chemical losses can be reduced by black liquor oxidation or gas scrubbers, while digester losses may be reduced by by-product recovery, solution of gases in liquor in a black liquor oxidation tower, or oxidation. Lime kiln control devices include wet scrubbers and bag filters while on power boilers electrostatic precipitators, cyclones, and wet scrubbers may be used. Procedures intended to reduce chemical losses also reduce environmental pollution.

TABLE 1

SOURCES OF AIR-BORNE GASEOUS AND PARTICULATE
EMISSIONS IN THE KRAFT PROCESS⁶

Gaseous		Particulate	
Importance	Source and Compounds	Importance	Source and Compounds
Major	Recovery furnace - H_2S , SO_2 , and some CH_3SH and $(\text{CH}_3)_2\text{S}_2$. Evaporators - H_2S and some CH_3SH and $(\text{CH}_3)_2\text{S}_2$. Digesters - H_2S , CH_3SH , $(\text{CH}_3)_2\text{S}$, and $(\text{CH}_3)_2\text{S}_2$. Lime kiln - some H_2S . Auxilliary power boilers (including bark burning) SO_2 , NO_2 .	Major	Recovery furnace - Na_2SO_4 and Na_2CO_3 fumes. Evaporators - none. Digesters - none. Lime kiln - CaO dust. Auxilliary power boilers (including bark burning) Fly ash.
Minor	Smelt dissolving tank. Lime slaking. Lime mud filter. Pulp washers.	Minor	Salt cake and lime unloading systems.

Odor reduction may be achieved through black liquor oxidation, absorption of gases in water or caustic spray, chlorination, or burning. Black liquor oxidation and oxidation with chlorine are, to date, the most practical systems for odor reduction. One progressive west coast Kraft mill stores its dilute digester gases in a vaporsphere until a sufficient amount is collected to be passed through a chlorination system.⁶ Minor losses from dissolving tank, lime slaker, lime filter, or pulp washers are seldom treated. The ideal piece of control equipment is one which will recoup initial investment quickly by chemical savings or by-product recovery.

Black liquor oxidation prior to concentration is effective in reducing volatile sulfur loss in multiple-effect and direct-contact evaporation. The idea was first patented by the Swedish engineers Bergstroem and Trobeck. It is believed that black liquor oxidation transforms the inherent malodors into products which are less volatile and do not give rise to foul-smelling decomposition products. Because of the conservation of sulfur in the recovery system, the amount of sodium sulfate or sulfur make-up is decreased. This in turn decreases the percentage of sodium carbonate present in the green liquor which, therefore, reduces the quantity of lime needed for causticizing. By conserving sulfur in the system, black liquor oxidation produces a white liquor with high sulfidity (i.e., percentage of sodium sulfide in the active chemicals) which means a better, more buffered cooking cycle. Black liquor oxidation also improves the suitability of precipitated lignin for by-product use and enables the evaporators to be operated more uniformly and efficiently.

To date, the main drawbacks of black liquor oxidation have been the expensive equipment cost and excessive foaming attributed to the soap-like materials present in the liquor. Because of these drawbacks at least part of the cost of such a system is frequently justified on the basis of reduced odor and corrosion. At the present time some full-scale black liquor oxidation units are operating in the north and northwest United States, Canada, Mexico, and Sweden, although the mechanisms of the process are not thoroughly understood.

Oxidation using pure oxygen rather than air has been suggested by previous researchers.^{7, 8, 9} A closed cycle is necessary economically to ensure that all of the oxygen introduced eventually is assimilated by the black liquor. In such a system the foaming problem is minimized if contact time is sufficient to enable any entrained bubbles to be completely absorbed. Defoaming agents become unnecessary and equipment size can be minimized since high oxygen tensions will shorten contact time. Attempts have been made to add oxygen directly to a digester towards the end of a cook.⁹ This study was abandoned at the bench scale primarily because the oxygen costs exceeded the salt cake and lime savings.

Under present economic conditions black liquor oxidation in general is a marginal operation. Future adjustments in chemical prices, increased expansion, and social pressures caused by environmental pollution could change this situation radically. The principal advantage of the oxygen system over the air system is that the gas can be introduced directly into existing equipment, such as pipe lines or storage tanks, and achieve a degree of oxidation without expensive equipment.

At present black liquor oxidation has not met with success in the southeastern United States partly because of the pronounced foaming tendencies of southern Kraft black liquor. Although many equipment patents have been registered, voids still exist in the basic understanding of the mechanisms of the process. The technology has advanced to a point where further refinements are difficult without a better understanding of the fundamental aspects of the problem. Although it generally is accepted that black liquor oxidation reduces volatile sulfur losses and, hence, atmospheric pollution, the true reasons underlying this stabilization are unknown.

Technical information applicable to the problem can be divided into two general categories: the application and technology of black liquor oxidation, and the chemistry of pure sulfur compounds. Neither the chemical engineering nor the pure chemistry approach adequately answers certain basic questions concerning black liquor oxidation. These questions are: what changes occur during oxidation; in what quantities do these changes occur; and why do the changes occur?

The previous research reported in the literature has been conducted for very specific process applications, hence much of this work cannot be applied comprehensively to the general case of black liquor oxidation without verification and modification.

Dealing with black liquor presents some unique technical problems. The black liquor contains approximately 5 per cent inorganic and 10 per cent organic matter, and the interaction between the mineral and the complex organic constituents is largely unknown. There are

some controversial factors and more knowledge about them is necessary before the mechanisms of black liquor oxidation can be truly understood.

The main purpose of black liquor oxidation is to stabilize the volatile sulfur compounds in the liquor. The effectiveness of this oxidation in reducing gaseous losses depends on the method and degree of oxidation. Oxidation stabilizes the liquor for evaporation but some gases may be lost during oxidation.

Advantages and Disadvantages of Black Liquor Oxidation

Summarizing the advantages and disadvantages of black liquor oxidation, the advantages include:

1. Reduction of salt cake make-up and lime required for causticizing.
2. Reduction of corrosion in multiple-effect and direct-contact evaporators and scrubbers as well as at the plant site.
3. Better and more buffered cooking liquor.
4. Improved by-product recovery.
5. Reduction of odors released from evaporators.

The disadvantages are:

1. Capital investment in equipment which will not directly increase production.
2. Additional operational costs to maintain oxidation equipment.
3. Increased chemical costs if pure oxygen is used.

CHAPTER II

PURPOSE AND SCOPE

Purpose

This work was conducted as a fundamental research project in atmospheric pollution control at the Air Pollution Research Laboratory, University of Florida. The purpose of the study was to investigate completely the oxidation of Kraft black liquor using pure oxygen and a mixture of oxygen plus ozone. The fate of the principal sulfur compounds during oxidation was determined and their technological significance evaluated. The technical and economic feasibility of mill scale oxidation using pure oxygen was discussed. The possibilities of eliminating pulp mill odors with ozone was also investigated.

Through this paper the relative importance of the parameters controlling black liquor oxidation has been established. Where conflicting reports existed in the literature, experimentation was conducted to define the process accurately. It is hoped that in putting black liquor oxidation on a more quantitative basis, this study aids the development of a commercial system applicable to Kraft mills in the southeastern United States.

Scope

Black liquor oxidation was investigated under a variety of conditions to determine the effect of different parameters on the process.

The principal physical and chemical parameters examined were:

1. Temperature.
2. Oxygen partial pressure.
3. Method of contact.
4. Oxidizing agent.

The practical temperature range considered was from 60°C to 90°C. Reaction pressures were not raised above one atmosphere since previous studies^{9, 10} indicated that elevated pressures were conducive to excessive oxygen consumption. Several different methods of contact were used and the oxidation efficiency of oxygen, and oxygen enriched with ozone were contrasted.

By varying the pertinent parameters, the following areas were investigated:

1. The nature of the predominant inorganic reactions that occur during oxidation and the effect of temperature, oxygen pressure, and method of contact on the products of reaction.
2. The precipitation of elemental sulfur from the black liquor.
3. The completeness of these predominant reactions and a sulfur balance for the entire system.
4. The degree of reversibility of these reactions.
5. The kinetics of oxidation and the effect of temperature, oxygen pressure, method of contact, and oxidizing agent on the rate of reaction.
6. The oxygen requirements of the black liquor and the utilization thereof.

7. The catalysis of sodium sulfide in black liquor.

8. The emission of oderiferous gases during oxidation.

9. The elimination of these gases by oxidation with ozone and the application and approximate cost of similar oxidation to other odor sources.

10. The application and the approximate costs of a mill scale, pure oxygen oxidation system.

CHAPTER III

SURVEY OF PREVIOUS WORK

Literature Survey

The idea of stabilization of some of the sulfur compounds in Kraft black liquor was first suggested by M. G. Schmitt¹¹ in 1938. Schmitt noted that in the recovery operation sulfur losses exceeded sodium losses by a ratio of four to one. The high sulfur loss was thought to be due to thermal instability of residual sodium sulfide in the black liquor. To remedy this situation Schmitt proposed aeration of the black liquor as well as other methods of treatment.

Since its inception, most of the work on black liquor oxidation has been conducted by a few groups of investigators in Sweden, Canada, and the United States. To date, studies of black liquor oxidation have been aimed primarily at reducing chemical make-up rather than odor or atmospheric pollution control. From this aspect the economics of the system have been marginal.

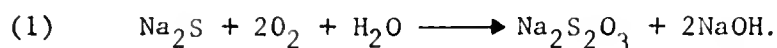
In the period between 1939 and 1942, Bergstroem and Trobeck¹¹ studied the changes that occur in black liquor after storage. They found that at elevated temperatures in the presence of air the sulfide content decreased. Based on this work, Bergstroem pioneered the first installation of a black liquor oxidation system at the Norrsundet, Sweden, mill in 1952. Bergstroem and Trobeck¹¹ reported reduction in sulfur losses from 26 to 10 per cent at this installation. They also

noted decreased evaporator corrosion, increased white liquor sulfidity, increased viscosity, and no decrease in heat value of black liquor. They found, however, that oxidation efficiency dropped off when the solids content went above 30 per cent.

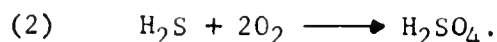
The Bergstroem-Trobeck system was developed in conjunction with high-vacuum evaporation of black liquor to dryness (i.e., 10 per cent moisture). The weak black liquor was run into a tower containing perforated shelves. Air blown into the bottom of the tower converted much of the liquor into foam which was carried up through the unit and out into a cyclone to separate foam and droplets. The liquid from the cyclone was evaporated to dryness and burned. A number of Swedish, Canadian, and American patents have been obtained covering the Bergstroem-Trobeck equipment.

A Bergstroem-Trobeck oxidation system has been installed in the Kraft mill of Loreto and Pena Pobre near Mexico City and its operation investigated by Trobeck, Lenz, and Tirado¹² in 1959. In 1961, Tirado et al.,¹⁰ conducted bench scale oxidation studies using air under pressure. The reactor consisted of a vertical pipe with an air diffuser at the bottom. Liquor and air in variable quantities were fed through the bottom and the products of reaction escaped through a pressure relief valve at the top. At 50 pounds per square inch and 149°F the liquor was well oxidized if air was supplied at a rate of 2.3 times the theoretical requirement. The oxidation of black liquor by air at 25 to 75 pounds per square inch showed promise, especially regarding the stabilization of mercaptans which are difficult to oxidize in conventional processes.

Trobeck^{11, 13} stated that complete oxidation would eliminate sulfur lost as hydrogen sulfide and mercaptans in the evaporators. He suggested that the sulfide present as sodium sulfide may be oxidized according to the following formula:



The author mentioned, however, that it is likely that some of the hydrogen sulfide was tied up in the liquor in the form of organic compounds. Trobeck said that corrosion was caused by gaseous hydrogen sulfide which oxidized to form droplets of sulfuric acid in the evaporator tubes:



Reducing the amount of hydrogen sulfide in the evaporators increased the tube life almost ten-fold.

Trobeck also presented data on the oxygen absorbed during oxidation of black liquor (see Figure 2).

The sharp increase in oxygen uptake after 30 minutes was accompanied by a decrease in liquor heating value which indicated oxidation of organic matter. Since this loss in heat value was not found in less than 30 minutes of oxidation, it was concluded that oxidation of sulfide is possible without wasteful destruction of organic matter.

Tomlinson¹⁴ and co-workers in Canada developed a nonfoaming oxidation tower as part of their recovery process. Tomlinson placed great emphasis on the fact that hydrogen sulfide was lost from the concentrated black liquor in direct contact (disc, cyclone, or cascade) evaporators due to the reaction of sodium sulfide with acidic gases

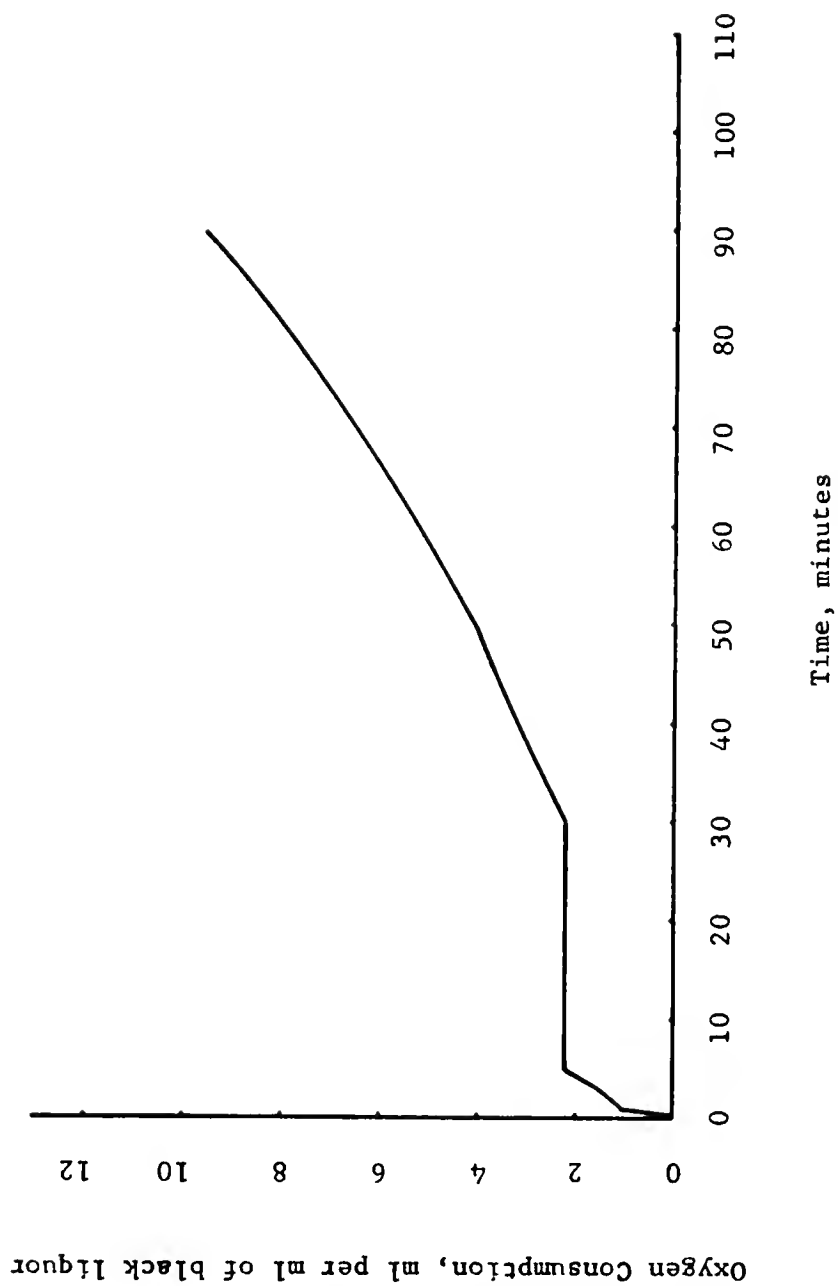


Fig. 2.-Utilization of oxygen by black liquor.¹³

such as sulfur dioxide, sulfur trioxide, and carbon dioxide. They found that when a completely oxidized black liquor was evaporated by hot flue gases in a venturi scrubber, the effluent gas contained only 180 parts per million of hydrogen sulfide.

Tomlinson et al., suggested that stabilization was achieved because dissolved hydrogen sulfide was oxidized to sulfur, sulfites, or sulfates which are no longer subject to destructive hydrolysis. Laboratory pilot plant work employed a counter-current tower packed with coke or Raschig rings and the optimum reaction temperature was found to be about 70°C. Designs based on this study supplied five times the theoretical quantity of air necessary to react with the sodium sulfide. Full-scale units have been erected in Windsor and Marathon, Canada. At Marathon, the gaseous effluent from the counter-current oxidation tower is fed into the recovery furnace and the residual odorous material burned. Several United States and Canadian patents have been issued covering these systems.

A chemical recovery system of the Tomlinson type, including black liquor oxidation, was installed at the South African Pulp and Paper, Ltd., mill in Springs, S. A.¹⁵ Eucalyptus is one of the species being pulped and it has been noted that isopropyl mercaptan and isopropyl disulfide are detectable in digester relief gases. Hisey reported that oxidation tests at Springs showed 85 per cent sulfide reduction and that 48 hours additional contact did not completely fix the remaining sulfur.

A combination oxidation and absorption tower used to strip sulfurous gases from the digester exhaust has been investigated.

Collins¹¹ passed noncondensable evaporator and digester gases along with fresh air into an experimental Tomlinson oxidation tower. He noted that the odor of both the gas and the black liquor was reduced while the biochemical oxygen demand of the liquor was not markedly decreased.

In addition to the Bergstroem-Trobeck and Tomlinson systems for oxidizing black liquor, it has been recognized that oxidation occurred in the Industrikemiska Aktiebolaget^{11, 16} (INKA) system used for evaporating sulfate liquor. This system was independently patented by Öman and Göth, and Nauclér and Ledin in 1927 and 1928, respectively. In the INKA evaporator the black liquor was heated indirectly by the recovery furnace stack gases; the hot liquor then flowed over a perforated plate through which dry air was blown. The dry air evaporated the black liquor and oxidized it to a certain extent. Actually, many of the INKA patents concerned the design of an aerating and evaporating device which brought the liquor in contact with air without causing excessive foam. The sodium sulfide in the liquor was reduced approximately 80 per cent in its 20 passes through the INKA evaporator.

A detailed study of black liquor oxidation was carried out by Bialkowsky and DeHaas^{17, 18} of the Weyerhaeuser Timber Company. These workers noted a very definite decrease in sulfide content when black liquor was passed through the pulp washers. From their observation that additions of sodium sulfide to oxidized black liquor proceeded to oxidize rapidly and from unpublished polarographic data, the authors concluded that organic compounds in the black liquor catalyzed the oxidation reaction. They also found that more oxygen reacted with the black liquor than was necessary to oxidize the sulfide to thiosulfate according

to reaction 1. No increase in sodium hydroxide was detected, however, and it was thought that this increase may have been masked by the buffering action of the organic compounds. Bialkowsky and DeHaas also investigated the addition of air to a pilot plant digester. They found that the sulfide concentration of the black liquor was lowered and the bleachability of the pulp was increased.

The basic oxidation studies of Bialkowsky and DeHaas were carried out in a concurrent-flow glass tower. Using "wetted wall" surfaces with careful control of the temperature, humidity, air, and liquor flow rates, they determined the optimum transfer coefficients for oxidizing the sulfide. They found that foaming decreased and oxygen consumption increased as the temperature rose. Studies in a cascade-type evaporator showed that unoxidized liquor lost all of its hydrogen sulfide while oxidized liquor lost little hydrogen sulfide when evaporated to dryness. Next, the possibility for absorbing and oxidizing noncondensable gases from digester relief and blow gases with black liquor was studied in a laboratory oxidation tower. Hydrogen sulfide, methyl mercaptan, and dimethyl sulfide were mixed with air and passed through a packed tower. Fresh black liquor was passed concurrently through the packed column. Hydrogen sulfide was completely absorbed and oxidized; 5 per cent of the methyl mercaptan passed unchanged, 40 per cent left the tower as methyl di-sulfide, and the rest was absorbed in the liquor. Over 90 per cent of the methyl di-sulfide passed through the tower unchanged.

Other tests showed that when temperature was increased to around 250°C, some hydrogen sulfide was evolved from the black liquor in spite

of the fact it did not contain any residual sodium sulfide. These results indicated that a reduction of hydrogen sulfide losses could be expected as far as the direct contact evaporators were concerned, but any localized overheating in the evaporators and high temperature combustion in the furnace would release hydrogen sulfide gas.

Wright and associates¹⁸ at the British Columbia Research Council began work on odor control in 1948. Methods of analysis for hydrogen sulfide and methyl mercaptan were developed and the kinetics⁶ of the oxidation process were studied using a respirometer. The effect of interfacial mass transfer was minimized by making the gas-liquid interface very large. This was achieved by absorbing black liquor on filter paper, thus presenting maximum surface area. They found that sodium sulfide and mercaptans in black liquor were oxidized readily and that the oxygen absorption continued indefinitely thereafter but at a steadily diminishing rate. Tests also showed that oxygen consumption increased with temperature in the range of 40°C to 90°C. Wright also indicated that 1 to 3 volumes of oxygen were needed to oxidize completely 1 volume of black liquor. Since the black liquor contained approximately 1.7 grams per liter of sodium sulfide, this meant each mole of this sulfide consumed 2 to 5 moles of oxygen during oxidation.

It was found that with infinite area the oxidation of sulfur compounds still required from 2 to 3 minutes and hence nothing was gained by increasing the superficial area beyond a certain point.

To test laboratory data a pilot plant oxidation unit was built at the Port Alberni,^{19, 20} British Columbia, mill of Bloedel, Stewart, and Welch. Concurrent air and liquor flow was used in the tower and

noncondensable digester gases were added to the air supply. These gases were practically completely absorbed and the exit air carried little, if any, Kraft odor. This statement contradicted the findings of Bialkowsky and DeHaas.

In 1959, Murray⁷ at the British Columbia Research Council published a comprehensive study of the kinetics of oxidation of Kraft black liquor using both air and pure oxygen. Murray reported that the maximum rate of oxidation occurred at 72°C using pure oxygen and that sulfur formation was favored by temperatures below 80°C, low sulfide concentration, and high oxygen pressures. Murray found that oxidation rates were higher when pure oxygen rather than air was used, but a five-fold increase in oxygen pressure did not bring about a proportional increase in oxidation rate. It was noted that storing oxidized black liquor at elevated temperatures in the absence of air caused some of the sulfide to be regenerated. This was especially true when sulfur was an oxidation product. It was also reported that oxidation rates were not greatly affected by changes in solids content. Experiments showed that an increase in thiosulfate concentration reduced the black liquor oxidation rate while an increase in sodium hydroxide increased the oxidation rate. The addition of elemental sulfur to a digester produced sulfide according to equation 3; the over-all effect was to lower the sodium hydroxide concentration and increase the thiosulfate and sulfide concentrations.



On the basis of the kinetic data Murray concluded that the oxidation takes place in two definite steps: the first a rapid oxidation and then

a slower reaction. Therefore, he suggested that a two-stage oxidation system should be more efficient than a one-stage system.

Collins^{11, 16, 22} published a series of papers on black liquor oxidation. On the basis of preliminary studies he presented data on the effect of oxidation on the sulfur compounds in black liquor (see Table 2). Collins found that the sulfide, thiosulfate, and sulfite oxidized to thiosulfate and sulfate. Collins also showed that chemical oxidation of black liquor with sodium peroxide was impractical. Based on the results of pilot plant studies at Thilmany, Wisconsin, Collins developed a commercial system for black liquor oxidation. In this system air was blown into the black liquor to form a stable foam. The oxidized foam was then collected in a cyclone and converted back into liquor. A material balance on the Thilmany evaporators indicated that the use of oxidized black liquor greatly reduced sulfur losses.

A comprehensive literature review published by Collins¹¹ in 1953, included most of the significant basic and related papers on sulfate black liquor oxidation. He mentioned an early patent in which alkaline waste liquors were purified by concentrating and heating with hot air in the presence of caustic until the organic substances carbonized. Addition of an oxidizing agent such as saltpeter was also suggested. Collins noted another source which pointed out that sodium sulfide in weak wash water discharged to the sewers was partially oxidized by the dissolved oxygen in the water. He also mentioned Basberg who discovered that at room temperature, in the absence of air, black liquor sulfide content did not change after 5 weeks of storage.

TABLE 2

EFFECT OF OXIDATION ON THE SULFUR COMPOUNDS
IN A NORTHERN BLACK LIQUOR²²

Material	Concentration	
	in Fresh Liquor Grams per Liter	in Oxidized Liquor Grams per Liter
Na ₂ S	9.01	1.02
Na ₂ S ₂ O ₃	4.07	11.75
Na ₂ SO ₃	0.18	0.00
Na ₂ SO ₄	3.97	5.48
Total Sulfur (by analysis)	6.56	6.45
Total Sulfur (by addition)	6.29	6.42

According to Collins,¹¹ Venemark stated that some of the sulfur compounds in black liquor were subject to air oxidation at room temperature. Venemark also reported that when evaporation was carried out in direct contact with flue gases, sulfur losses occurred due to the action of acidic gases on the alkaline black liquor.

In his literature survey Collins¹¹ discussed the laboratory findings of Bozza and Colombo. Their kinetic studies showed that the oxidation of sulfide was a first order reaction, but the oxidation of mercaptan was intermediate between a first and a second order reaction. To determine the retention of sulfur in black liquor after oxidation of the liquor, they distilled various samples in a current of nitrogen and analyzed the gases evolved. Oxidation resulted in the reduction of the amount of hydrogen sulfide lost during distillation but mercaptans were not affected.

Heath, Bray, and Curran²² referred to the early work of Klason and Segerfelt in which the oxidation of black liquor when stored was first noted. This observation was never followed up and no attempt was made to apply black liquor oxidation.

Fones and Sapp⁹ oxidized Kraft black liquor at digester temperatures using pure oxygen. Their experiment was divided into three phases: the oxidation of pulp alone; the oxidation of pulp and black liquor at the end of a normal Kraft cook; and the oxidation of black liquor alone. The first two phases produced undesirable reduction in pulp quality. On oxidizing the black liquor alone at 100 to 120 pounds per square inch, the sodium sulfide was oxidized to sodium thiosulfate, which in turn was oxidized to sodium sulfate (see Figure 3). Unfortunately, a sulfur

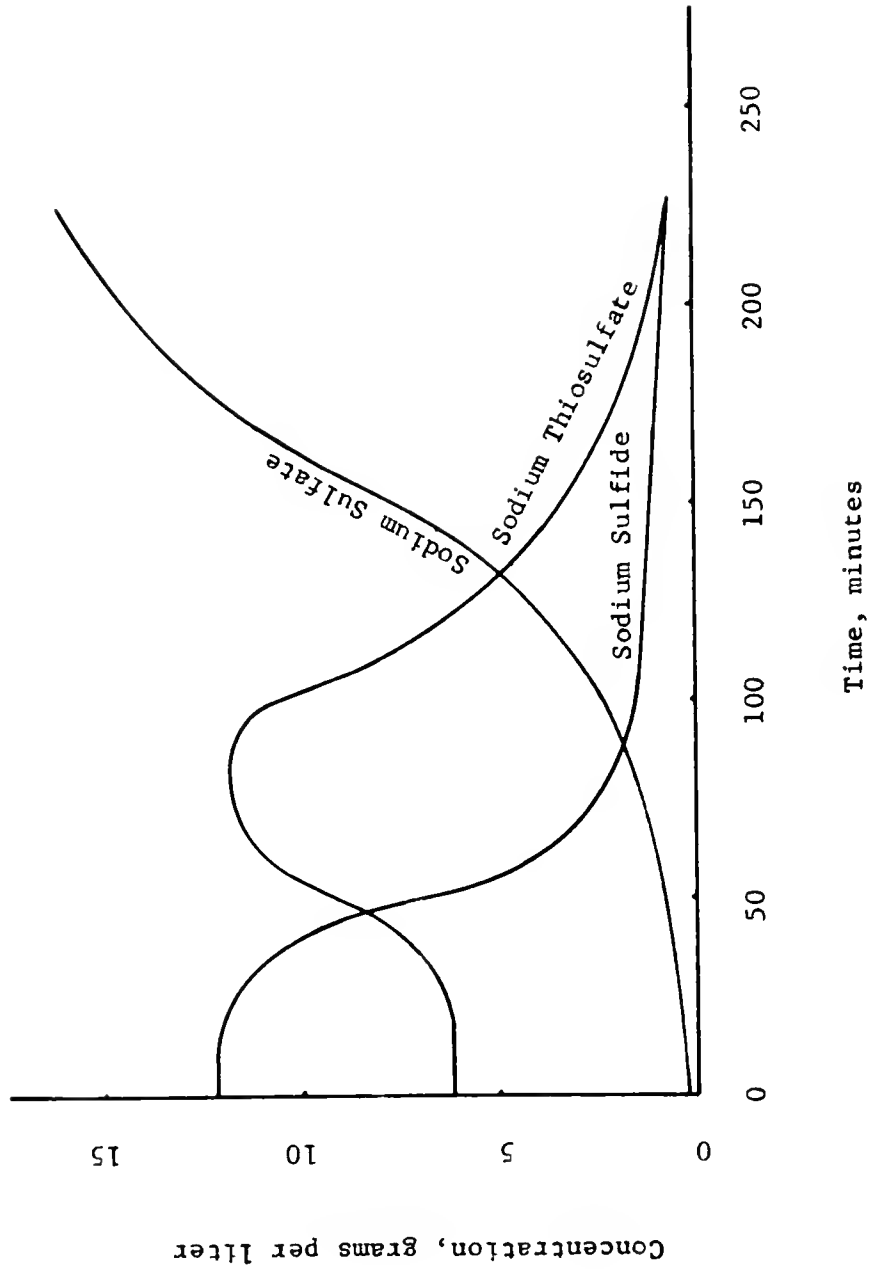


Fig. 3.-Fate of sulfur compounds during oxidation at 100 - 120 psi pressure using pure oxygen.

balance on the data in Figure 3 does not account for all the sulfur compounds (see Table 3). After 150 minutes only 76 per cent of the sulfur initially present as sulfide was accounted for by the thiosulfate and sulfate formed. After 217 minutes, however, all of the sulfur was accounted for. It would appear that some other compound or compounds, either organic or inorganic, were formed during oxidation.

Conclusions Based on Previous Literature

On the basis of the literature survey of the information available on black liquor oxidation, certain conclusions can be drawn:

1. Although the possibility of oxidizing black liquor has been known for at least 20 years, little theoretical information is available on the basic mechanisms of the process. The majority of the literature covered the application of a few basic ideas to specific mill problems.

2. Full scale units have been successfully installed and operated in areas other than the southeastern United States.

3. The principal reason for installation of a black liquor oxidation system is to reduce chemical losses and corrosion rather than to improve cooking liquor or reduce atmospheric pollution.

4. Knowledge of the chemistry of the stabilization of the sulfur compounds in black liquor is indefinite. It is suspected that the dissolved organic material catalyzes the oxidation of the sulfide but little has been reported about this mechanism.

5. The relative importance of the physical parameters of the system, such as temperature, contact method, and choice and quantity of oxidizing agent, have not been reported.

TABLE 3

MOLAR SULFUR BALANCE OF DATA IN FIGURE 3

Time	Concentration			Sum	Percentage of the Sulfur Accounted For
	Sulfide Expressed as Moles per Liter Sulfur	Thiosulfate Expressed as Moles per Liter Sulfur	Sulfate Expressed as Moles per Liter Sulfur		
0	0.155	0.077	0.058	0.290	100.0
27	0.146	0.080	0.063	0.289	99.7
38	0.098	0.076	0.068	0.242	83.4
45	0.107	0.095	0.070	0.272	93.8
55	0.069	0.128	0.077	0.274	94.5
62	0.055	0.134	0.070	0.259	89.3
78	0.026	0.150	0.074	0.250	86.2
95	0.023	0.136	0.084	0.243	83.8
114	0.017	0.099	0.118	0.234	80.7
150	0.014	0.039	0.168	0.221	76.2
191	0.010	0.019	0.250	0.279	96.2
217	0.006	0.006	0.278	0.290	100.0

6. There is some doubt as to whether or not black liquor can be oxidized without the emission of odors.

7. There is also some doubt as to whether or not black liquor oxidation using pure oxygen is technologically or economically feasible.

The work on black liquor oxidation over the past 20 to 30 years has added knowledge as well as conflicting information to the technology of the pulp and paper industry. Black liquor oxidation as a means of reducing chemical losses and atmospheric pollution from the recovery cycle of the Kraft process has definite potential. In some instances oxidation has been made to work, while in others, technical and economic limitations have hindered its application.

Oxygen, if properly utilized, may prove feasible on a mill scale although it is a more expensive oxidizing agent than air. The potential advantages of an oxygen system over an air system are:

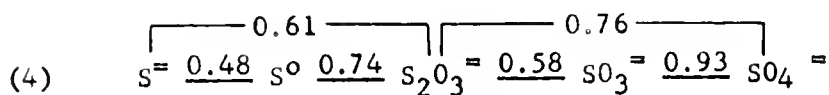
1. The elimination of the foam problem.
2. Higher oxygen pressures over the liquor, which will decrease the contact time and hence the size of the equipment.
3. Improved by-product recovery from black liquor.

CHAPTER IV

THEORY

Oxidation States of Sulfur

Sulfur in various degrees of oxidation is found in black liquor. The more common oxidation states with their corresponding oxidation potentials²⁴ in basic solution are shown below:



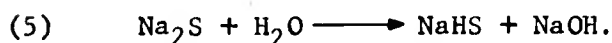
Polysulfides are also stable in alkaline solution but have not been included in the above diagram because their oxidation potentials are indefinite. Polysulfides are intermediates between sulfide and elemental sulfur and include the disulfide, $\text{S}_2^=$, and the tri-, $\text{S}_3^=$, tetra-, $\text{S}_4^=$, and penta-, $\text{S}_5^=$, sulfides. The couples shown in equation 4 are not subject to rapid reversibility and hence they cannot be used to calculate equilibrium constants.

Other oxidation states of sulfur include hyposulfite, $\text{S}_2\text{O}_4^=$, dithionate, $\text{S}_2\text{O}_6^=$, and the persulfates or thionates such as $\text{S}_3\text{O}_6^=$, $\text{S}_4\text{O}_6^=$, and $\text{S}_5\text{O}_6^=$. The problem of assigning polar oxidation states to these compounds is similar to that encountered with the polysulfides, since polar numbers are rather ambiguous because the sulfur atoms are linked by covalent bonds.

Evaporation of Sulfate Black Liquor

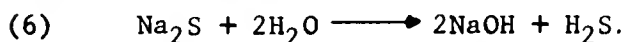
The active chemicals in Kraft white liquor are sodium sulfide and sodium hydroxide in concentrations of 15-30 and 40-65 grams per liter, respectively. During cooking the lignin and other noncellulosic portions of the wood are hydrolyzed into soluble compounds, freeing the fiber bundles. The products of hydrolysis include carbohydrates, alcohols, acids, thiolignin, mercaptides, and other soluble organics; the black liquor contains these constituents as well as unutilized sodium sulfide, sodium hydroxide, and other soluble mineral matter.

The sulfide in the liquor serves a dual purpose⁵ by buffering the system during cooking and by supplying sodium hydrosulfide (see reaction 5) which combines with lignin to form alkaline soluble thiolignin.

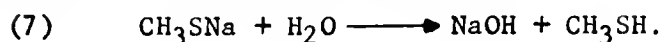


At the end of the cooking period the sodium sulfide is at least partially hydrolyzed and the concentrations of active chemicals (i.e., Na_2S and NaOH) are substantially reduced.

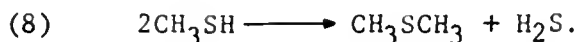
When the black liquor is concentrated in vacuum multiple-effect evaporators, some sodium sulfide is lost as hydrogen sulfide gas.¹¹



Another odorous evaporator loss, but a relative minor one⁶ in terms of volume, is methyl mercaptan. Methyl mercaptan and its sodium salt, sodium mercaptide, are formed by the reaction of hydrosulfide on free methyl groups during the cooking process. During evaporation some of the sodium mercaptide hydrolyzes and liberates methyl mercaptan.

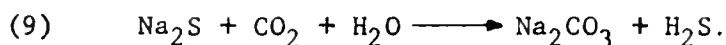


Methyl sulfide is another compound which is formed in the digesters possibly by the liberation of hydrogen sulfide from two molecules of methyl mercaptan.



The methyl sulfide and any other low boiling gases such as hydrogen sulfide or methyl mercaptan are stripped readily from the black liquor during vacuum evaporation.

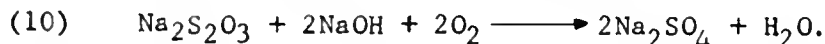
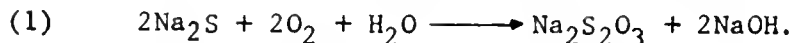
When unoxidized black liquor is passed through direct-contact evaporators and heated with flue gases containing carbon dioxide, hydrogen sulfide is lost.^{11, 14}



Thus hydrolysis, desorption, and reaction with acidic gases as shown in reactions 6 through 9 are the generally accepted causes of volatile sulfur losses during evaporation.

Black Liquor Oxidation

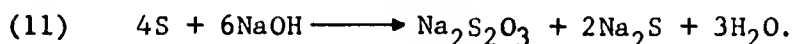
Black liquor oxidation reduces sulfur losses since the products formed are apparently nonvolatile and stable at evaporator conditions. Reactions 1 and 10^{9, 11, 13, 22} have been suggested to explain the formation of stable inorganic sulfur compounds.



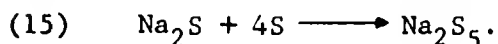
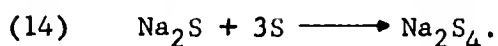
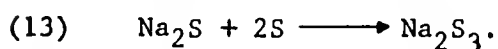
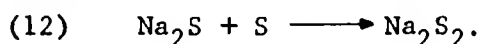
Neither sodium thiosulfate nor sodium sulfate is subject to destructive hydrolysis.

Prior to the experimental work, the following hypotheses were drawn from studies of the previous literature.

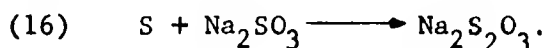
It seems likely that when black liquor is oxidized, several different oxidation states of sulfur will be formed. Certain compounds are more likely than others to be present in the strongly alkaline black liquor. Elemental sulfur, for example, is unstable in alkaline solution and slowly decomposes into sulfide and thiosulfate.^{24, 25}



It is unlikely, therefore, that elemental sulfur is a stable oxidation product of sodium sulfide. Further circumstantial evidence that elemental sulfur is not to be expected in black liquor is the fact that in an alkaline solution containing sodium sulfide and sulfur, the two compounds combine to form polysulfides according to reactions 12 through 15.²⁵

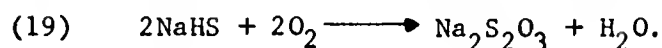
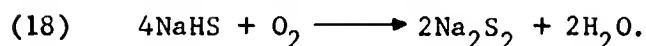
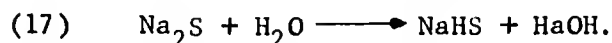


Sulfur also reacts with sodium sulfite to form sodium thiosulfate.²⁵



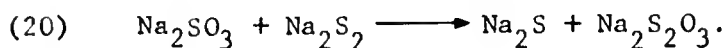
Under certain conditions, however, sulfur⁸ is formed and is apparently stable in the black liquor. The reasons for this sulfur formation will be investigated and discussed in this paper.

Yeoman²⁵ found that pure soluble metal sulfides in dilute solution slowly hydrolyze and in the presence of air produce both polysulfides and thiosulfates.



It may be possible that the sulfide in the black liquor reacts similarly when subjected to oxidation.

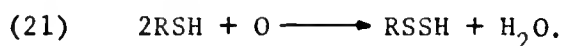
Sodium sulfite with an oxidation number of +4 is another compound which may be formed when black liquor is oxidized. Near the boiling point, however, sodium sulfite and disodium disulfide react quickly to form sodium sulfide and sodium thiosulfate.²⁵



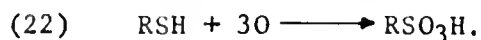
Hence, it is unlikely that both disodium disulfide and sodium sulfite exist simultaneously in the hot black liquor.

It is possible that only thiosulfate and sulfate, as suggested in reactions 1 and 10, are formed during oxidation. It is more likely, however, that a mixture of the many oxides of sulfur are formed during black liquor oxidation.

The free alkyl mercaptans, their derivatives, and salts are all subject to partial or complete oxidation. Under mild oxidation mercaptans form a stable disulfide.²⁶

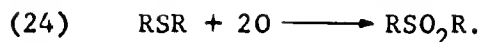
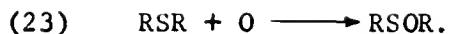


A more vigorous oxidation produces the corresponding sulfonic acid.²⁶



Pure oxygen normally oxidizes methyl mercaptan to methyl disulfide while a peroxide oxidizes methyl mercaptan completely to methyl sulfonic acid.

In a similar manner aliphatic sulfides are oxidized to sulfoxides and sulfones by mild and strong oxidation respectively.²⁶

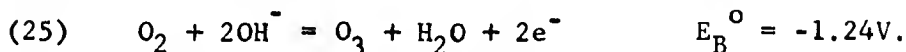


There is some doubt as to just how efficient black liquor oxidation is in attacking the mercaptan fraction. Tirado¹⁰ et al., reported that oxidation using air at a pressure of 70 pounds per square inch increased the oxidation of mercaptans from 45 to 85 per cent.

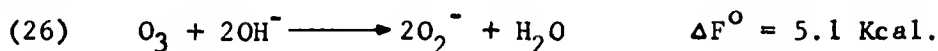
There is some question as to whether or not some of the oxidation products of methyl mercaptan are stripped from the black liquor during oxidation. It appears that methyl disulfide, CH_3SSCH_3 , and methyl sulfonic acid, $\text{CH}_3\text{SO}_3\text{H}$, with boiling points of 117°C and 160°C will remain condensed. Methyl sulfide, CH_3SCH_3 , methyl sulfoxide, CH_3SOCH_3 , and residual methyl mercaptan, CH_3SH , with boiling points of 38°C , 100°C , and 7.6°C , respectively, possibly will be volatilized from the liquor. during oxidation. This indicates that black liquor oxidation may emit some odoriferous sulfur gases.

Black Liquor Oxidation with Oxygen Plus Ozone

Stabilization of the soluble sulfur compounds may be accelerated by use of a stronger oxidizing agent than pure oxygen. A mixture of ozone and oxygen provides additional oxidizing power. Ozone is a strong electron acceptor and its oxidation potential is second only to fluorine.²⁴



Ozone has a very characteristic pungent odor and is more soluble than oxygen in a pure alkaline solution. Upon absorption in basic solution the ozone hydrolyzes and releases the powerful perhydroxyl ion.²⁴



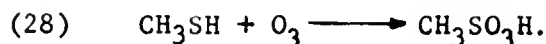
Ozone is produced by a high voltage corona discharge according to reaction 27.²⁵



It is thermally unstable and cannot exist at temperatures above 200°C. High concentrations decompose violently into oxygen with the liberation of heat.

Ladenberg²⁷ produced 86 per cent ozone in liquid oxygen, but Saunders and Silverman²⁸ found the equilibrium concentration of ozone at room temperature to be 16.5 per cent. The latter produced this concentration using a silent electrical discharge of 5.5 Kv, across a 2 mm gap, in an atmosphere of pure oxygen. Equilibrium was attained after a corona discharge of 70 to 90 minutes. Saunders and Silverman found that, using a 2 mm gap, 1.8 to 2.0 mg of ozone could be produced per coulomb of electrical energy--a value which was relatively independent of the potential used.

Ozone may also be useful in oxidizing odoriferous gases from a pulp mill. Ozone will oxidize methyl mercaptan directly to methyl sulfonic acid.^{25, 26}



Ozone will probably deodorize by oxidation other similar sulfurous organic gases.

Oxidation Kinetics

The oxidation of weak black liquor cannot be described by any simple chemical or absorption rate theory. The complexities of the oxidation occur because the temperature region of practical interest

is a transition region in which the products of reaction, sulfide concentration, and oxygen partial pressure act together to influence the oxidation rate.

Using the semi-empirical equation 29, the effects of chemical reaction and oxygen absorption can be separated.⁸

$$(29) \quad \frac{dC}{dt} = K (C + bP).$$

where: C = concentration of Na₂S in grams per liter at any time t, in minutes.

K = velocity constant for oxidation reaction.

P = partial pressure of oxygen in atmospheres.

b = constant representing the rate of oxygen absorption.

By varying experimental conditions the effect of temperature, oxygen pressure, method of contact, and oxidizing agent can be determined. If the gas-liquid interface offers no resistance to oxygen absorption, constant b will be zero and the oxidation is a first-order reaction. Similarly, if oxidation is independent of sulfide concentration, the reaction is of zero order, depending solely on the factor K (bP). These are the two limiting cases of equation 29 and in reality the actual situation probably lies somewhere between these two extremes.

CHAPTER V

EXPERIMENTAL

Equipment and Procedures

Experimentation on black liquor oxidation requires a ready supply of liquor, an oxidizing agent, and a method of bringing the two reactants into intimate contact.

The black liquor used in this study was obtained from the Hudson Pulp and Paper Company Kraft mill at Palatka, Florida. Black liquor was drawn off from a point between the pulp washers and the multiple-effect evaporators. It was collected in 5-gallon glass carboys which were sealed and allowed to cool. The space above the black liquor was filled with inert nitrogen or helium and the liquor was displaced as needed into a 4-liter flask. Analyses showed that liquor could be stored in these carboys up to five weeks with no apparent change in the initial sulfide concentration.

Compressed oxygen with a rated purity of 95 per cent was obtained in 200 cubic foot cylinders from the Matheson Company. When an oxidizing agent stronger than pure oxygen was required, a mixture of ozone and oxygen was produced and supplied to the system.

The ozone was produced by passing a stream of pure dry oxygen through a group of high voltage aluminum plates. The plates were insulated from each other with mica and a high voltage transformer was used to create a silent corona discharge between alternate plates.

A portion of the oxygen was ionized by the corona discharge and recombined as ozone. The ozone concentration was controlled by varying the voltage across the plates. The oxygen flow-rate was held constant at 450 cubic centimeters per minute. Concentrations from zero to 1450 parts per million of ozone could be produced in the generator shown in Figure 4.

The actual concentration of ozone being fed into the chamber was determined by passing a known volume of the ozone-oxygen mixture through an alkaline solution of potassium iodide. The quantity of ozone collected in the alkaline scrubbing solution was analyzed photometrically (see Appendix I).

The oxidation chamber consisted of a 12-liter cylindrical stainless steel chamber (see Plate 1 and Figures 5 and 6). Eight bolts around the periphery of the unit fasten the plexiglass lid to the chamber. A gasket made from 1/16 inch Cordet sheet packing provided a gas-tight seal between the plexiglass and the stainless steel. A fan which blows the oxygen down onto the exposed liquor surface and a stirring disc which agitates the liquor were both mounted on a stainless steel shaft. This pulley-driven shaft was mounted in a gas-tight bearing in the center of the plexiglass top. The shaft was turned at 98 revolutions per minute by a 1/30 horsepower, 110 volt, AC motor. The oxidizing agent was fed into the center of the chamber through an 11-millimeter glass tube and circulated by the fan. The liquor was introduced into the chamber through a funnel mounted on a length of 15-millimeter glass tubing. A three-way valve mounted on an auxiliary piece of 11-millimeter glass tubing served as a relief and exhaust valve.

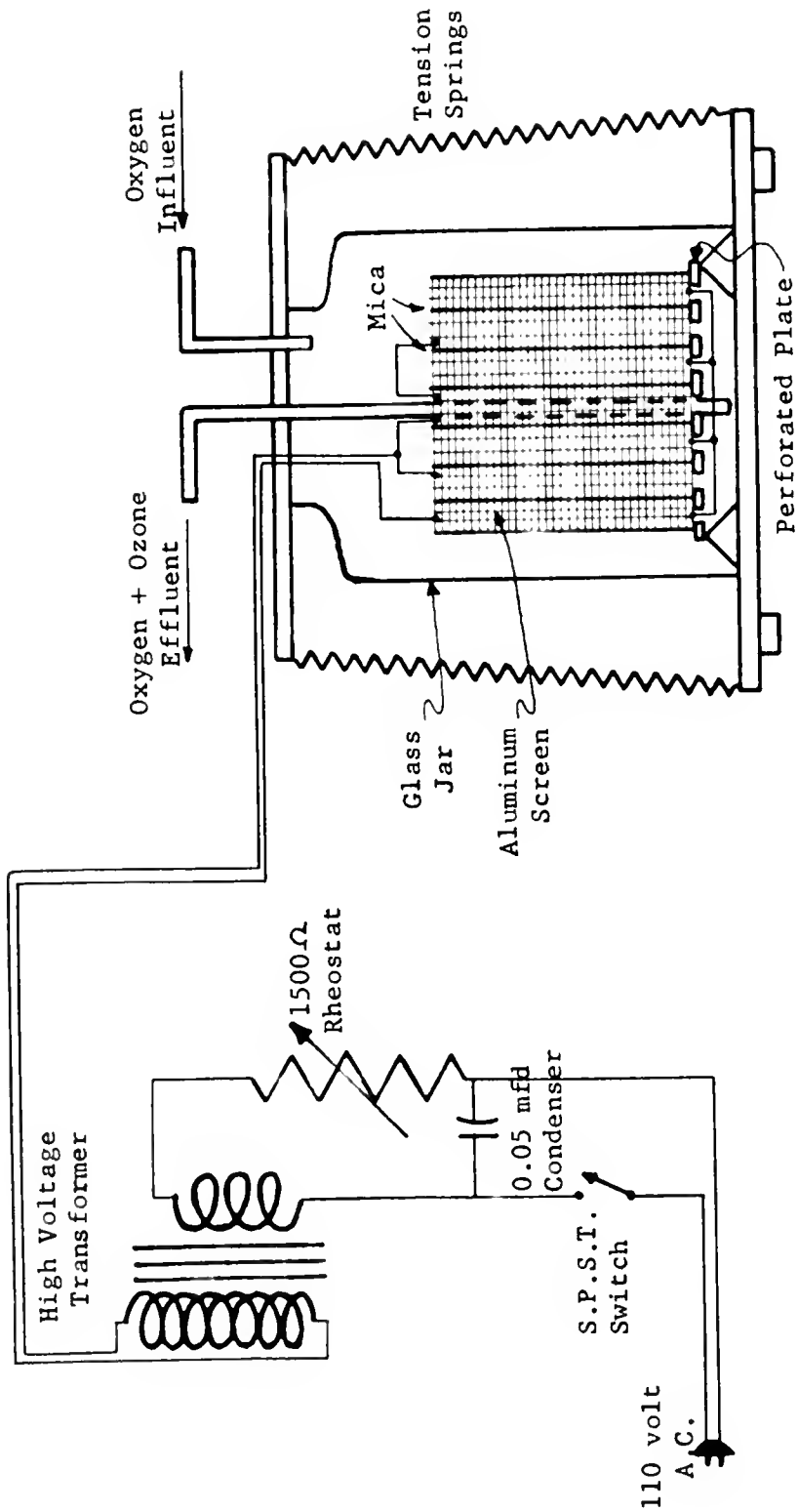


Fig. 4.-High voltage silent discharge ozone generator.



Pl. 1.-Photograph of experimental equipment. The principal components are: the oxidation chamber A; stirrer motor B; gas meter C; constant head relief valve D; storage carboy of black liquor E; compressed oxygen supply F; helium to deliver black liquor from carboy G; constant temperature bath H; thermostat controlled water heater I.

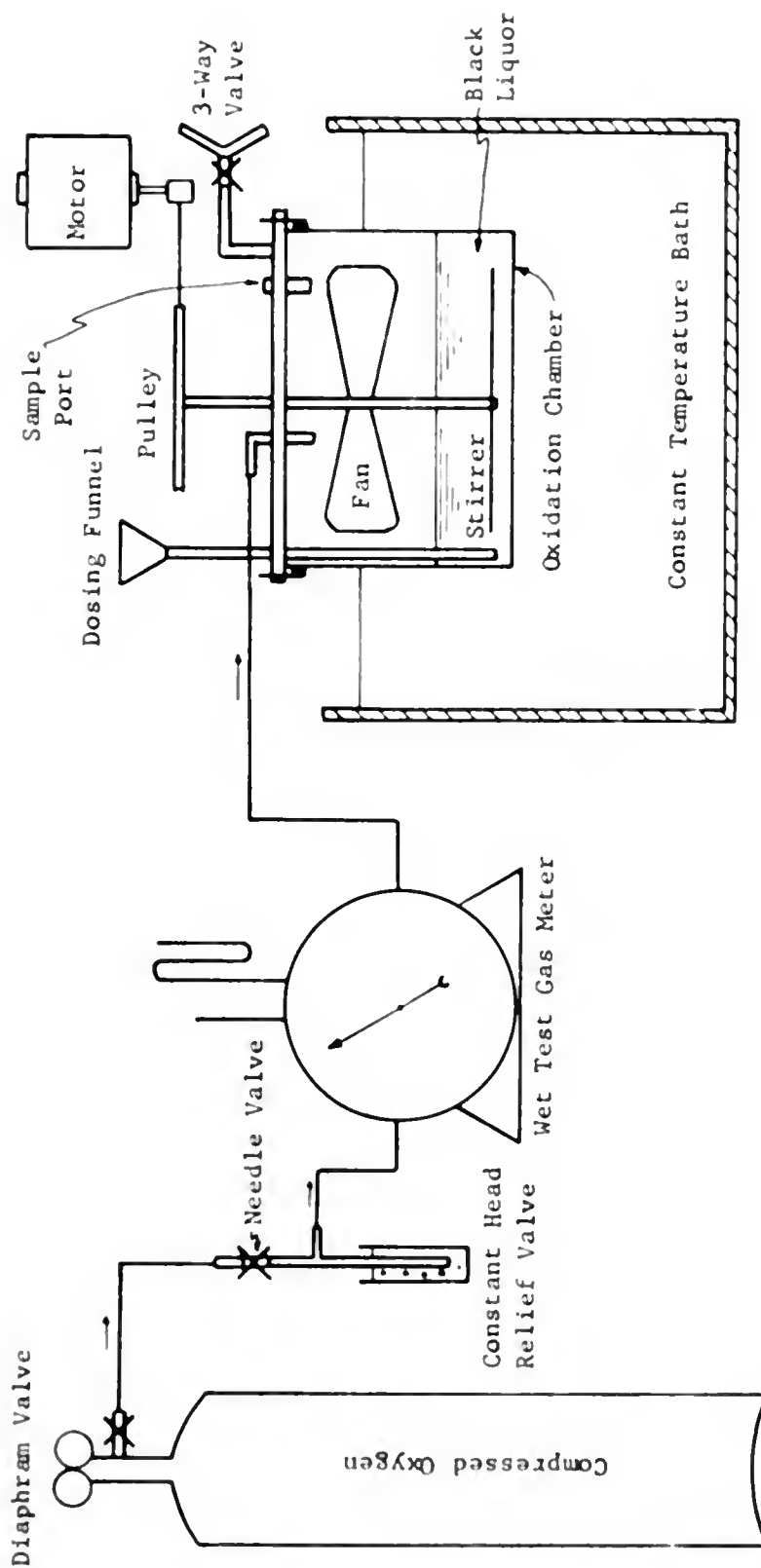


Fig. 5.-Flow diagram of static system oxidation equipment.

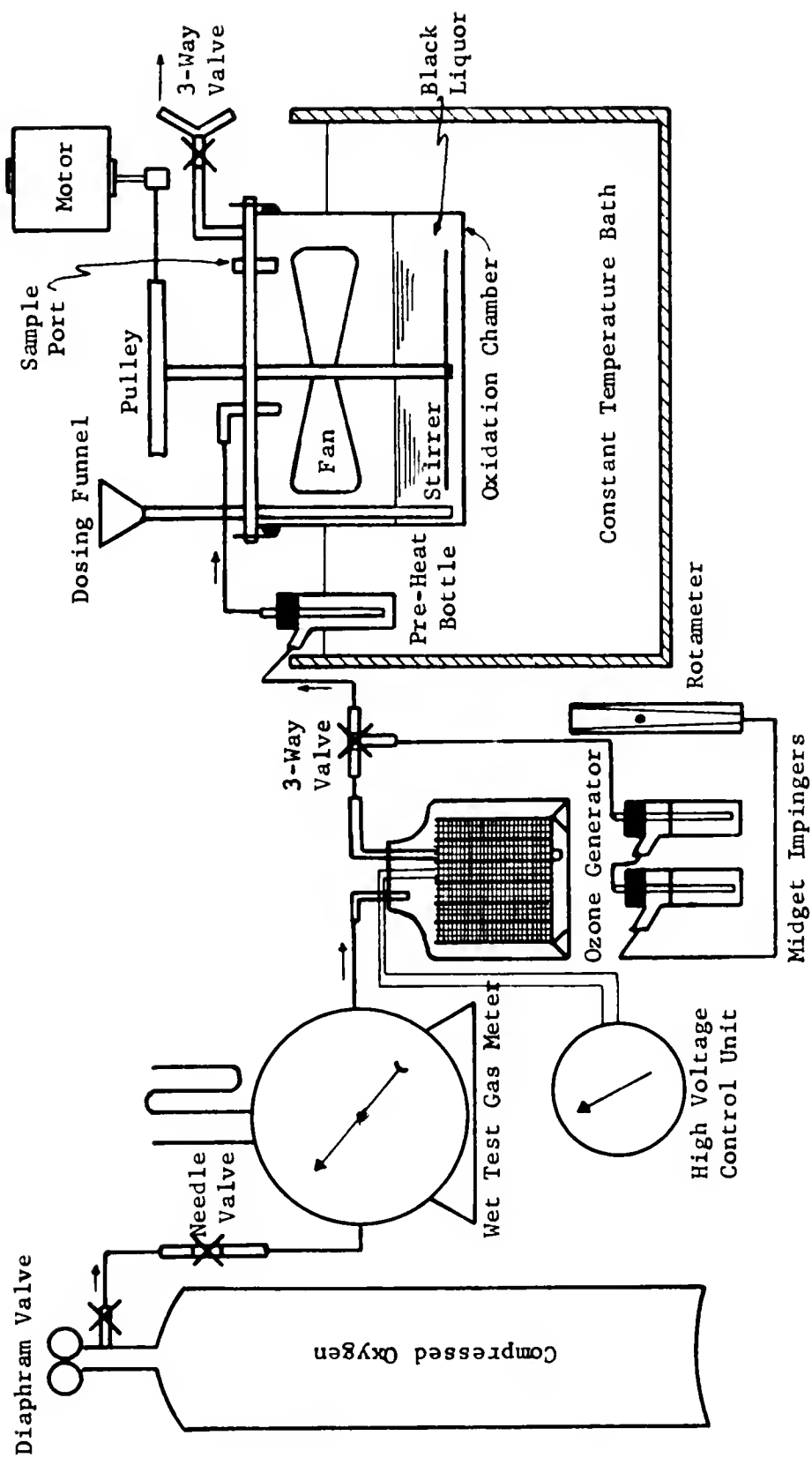


Fig. 6.-Flow diagram of dynamic system oxidation equipment.

Black liquor samples of 0.15 to 20.0 milliliters were withdrawn from the chamber through a sampling port with a hypodermic syringe. The sampling port consisted of a length of 15-millimeter glass tubing capped with a serum-bottle stopper. Liquor samples taken at different time intervals during oxidation were analyzed for sulfide, polysulfide, thiosulfate, sulfite, and sulfate.

The oxidation chamber was kept at a constant temperature by immersion in a thermostatically controlled water bath. A 2000-watt immersion heater kept the 15 gallons of bath water at the desired temperature, and the water was circulated by an electrically-driven stirrer.

Three methods, one static and two dynamic, were used to supply gas to the oxidizing chamber. In the static system the vessel was purged with oxygen, liquor poured in, and the chamber sealed. Oxygen was made available at a constant pressure of 50 millimeters of water and, as the liquor utilized the oxygen above it, more gas entered the chamber through a wet-test meter. The fluid in the meter previously had been saturated with oxygen. With this static system the volume of the consumed oxygen was determined. The static oxygen system is shown diagrammatically in Figure 5.

A dynamic or circulating system was also employed to oxidize the black liquor. An oxygen flow of 450 cubic centimeters per minute was used so that the gas above the liquor was changed approximately every ten to fifteen minutes. The oxygen flow rate was kept low in order to simulate static conditions as much as possible and not to upset the thermal equilibrium in the chamber. An oxygen-ozone mixture

was also supplied using this dynamic or circulating system (see Figure 6). When plain oxygen was utilized dynamically, the ozone generator was not energized.

Detailed descriptions of the operating procedures and testing sequences for the static and dynamic flow systems are given below.

Static Flow Procedures

1. Fix the oxidation chamber in place and bring the bath up to the desired working temperature.

2. Close the chamber, flush thoroughly with oxygen, and test for leaks.

3. Withdraw samples from the 4-liter black liquor flask and analyze for sulfide, polysulfide, thiosulfate, sulfite, and sulfate (see Appendix I).

4. Open the relief valve and quickly pour 4 liters of black liquor at room temperature into the oxidation chamber.

5. Reseal the chamber, start the stirrer, open the gas valve, and make oxygen available to the system at a constant head of 50 millimeters of water. The liquor is heated in the reaction chamber and temperature equilibrium is achieved in less than 10 minutes.

6. Read the wet-test gas meter at 5-minute intervals to determine the oxygen utilized by the black liquor. Withdraw liquor samples at 10- to 30-minute intervals during oxidation and analyze for sulfide, polysulfide, thiosulfate, sulfite, and sulfate.

Dynamic Flow Procedures

1. Fix the oxidation chamber in place and bring the bath up to the desired working temperature.

2. Close the chamber, flush thoroughly with oxygen, and test for leaks.

3. Open the relief valve and adjust the flow rate of oxygen or ozone-oxygen mixture to 450 cubic centimeters per minute.

4. Divert the ozone-oxygen stream from the chamber after equilibrium has been established in the ozone generator (after 2 to 5 minutes). Bubble the gas through two midget impingers containing alkaline iodide scrubbing solution. Analyze the contents of the impingers (Appendix I) and calculate the ozone concentration in the oxygen stream.

5. After sampling, re-direct the gas through the chamber and vent the exhaust to the hood. (If ozone is not used omit steps 4 and 5.)

6. Connect "freeze-out" traps to exhaust line to condense and concentrate the odorous sulfurous compounds in the off-gases. (If exhaust gases are not monitored for odors omit step 6.)

7. Withdraw samples from the 4-liter black liquor flask and analyze for sulfide, polysulfide, thiosulfate, sulfite, and sulfate (see Appendix I).

8. Quickly pour the 4 liters of black liquor at room temperature into the oxidation chamber.

9. Reseal the chamber except for the relief valve and start the stirrer. The liquor is heated in the reaction chamber and temperature equilibrium is achieved in less than 10 minutes.

10. Adjust the oxygen flow to 450 cubic centimeters per minute. Check this flow periodically throughout oxidation. Withdraw liquor samples at 10-to 30-minute intervals during oxidation and analyze for sulfide, polysulfide, thiosulfate, sulfite, and sulfate (see Appendix I).

Other oxidation studies were conducted using an impingement-type glass bubbler. This unit was mounted in the constant temperature bath and to minimize foaming the oxidizing gas impinged upon, rather than under, the surface of the black liquor. Placing the impinger tube under the surface of the liquor was found to be undesirable since the bubbles formed forced large quantities of foam into the exhaust line. This rapid "excess-air" technique was used to verify some tests conducted by a previous research worker in the field. The impinger was also used to supply small quantities of well-oxidized black liquor for miscellaneous other studies.

Analytical Methods

The methods of chemical analysis used were obtained from a variety of sources and in some cases had to be modified for use with black liquor. Methods for sulfate, thiosulfate, and sulfite in black liquor were obtained from TAPPI standards²⁹ T625m-48.

The determination of soluble sulfates in black liquor is a gravimetric analysis. The organic matter in a diluted sample of black liquor is precipitated by the addition of hydrochloric acid. These interferences are removed by double filtration. A dilute solution of barium chloride is added to the sample to precipitate barium sulfate. The precipitation is made in acidified solution near the boiling point. The precipitate is filtered off, washed with water, ignited to redness, and weighed as barium sulfate.

The thiosulfate and sulfite analyses are volumetric iodine-starch titrations. The sulfide and organic matter in the liquor is precipitated

with zinc carbonate solution and the precipitated interferences removed by filtration. The filtered sample is acidified with acetic acid and titrated with standard iodine solution to the blue-starch end point. This titration determines the total quantity of thiosulfate and sulfite present. A similar filtered sample is acidified and titrated with standard iodine solution after the sulfite has been destroyed by the addition of formaldehyde. This titration determines the total amount of thiosulfate present in the black liquor. The sulfite concentration is the difference between the two titrations. In general, the values for these titrations are somewhat high due to organic reducing agents invariably present. This is, however, the method recommended by TAPPI and apparently the best available at this time.

Sulfide is determined colorimetrically by the method of Strickland and Risk.³⁰ The dissolved sulfide reacts quantitatively with p-Phenylenediamine dihydrochloride in the presence of ferric chloride forming a deep purple color. The color is formed in a fixed volume of aqueous solution containing dye, oxidizing agent (ferric chloride), and wetting agent (alkyl dimethyl benzyl ammonium chloride). The sample is appropriately diluted and the absorption measured at 600 millimicrons against a similarly prepared blank. A reference absorption curve is prepared using a standard solution of sodium sulfide. This method was selected over the TAPPI standard method because it required less time and produced more reliable results.

Polysulfides are determined gravimetrically by a method modified from Scott's Standard Methods of Chemical Analysis.³¹ Soluble polysulfides quantitatively precipitate sulfur in a strongly acidified solution.

Interfering sulfides are precipitated with zinc chloride and interfering organic materials with hydrochloric acid; then both are removed by filtration. The pH is then lowered to 1.0 with hydrochloric acid to precipitate flowers of sulfur. The precipitate is filtered off, washed with water, dried, and weighed.

Ozone is analyzed colorimetrically using a variation of the method of Smith and Diamond.³² The oxidants are absorbed in an alkaline iodide solution and form hypiodite ion. The hypiodite quantitatively liberates iodine when the solution is acidified with acetic acid. The color is formed in a fixed volume of alkaline iodide solution and the absorption is measured at 352 millimicrons against a distilled water blank. A reference absorption curve is prepared using a standard solution of sodium iodate. Possible interferences in the oxygen stream include nitrogen dioxide, sulfur dioxide, and peroxides. The nitrogen dioxide interference is eliminated by adjusting the sample to the proper pH immediately before measuring the absorbence. The possibility of sulfur dioxide or any peroxides being present is unlikely since pure dry oxygen is used to produce the ozone.

Methods for total solids, specific gravity, percentage inorganic matter (sulfated ash), percentage organic matter, pH, hydroxide, and carbonate were also obtained from TAPPI standards²⁹ T625m-48.

The specific gravity and total solids are determined by weighing a known volume of black liquor before and after drying. The specific gravity is the ratio of the weight of one volume of black liquor to an equal volume of distilled water. The total solids are the oven-dry residue after all the water is completely driven off. This residue is

ashed, treated with sulfuric acid, ignited to redness, cooled, and weighed. The material remaining is the inorganic matter (sulfated ash), while the loss in weight is the volatile or organic matter.

The hydrogen ion concentration is determined on a pH meter equipped with a glass and a calomel electrode. The hydroxide concentration is determined from a potentiometric titration of a diluted liquor sample with standard hydrochloric acid to a phenolphthalein end point. The carbonate concentration is determined from a potentiometric titration of a diluted liquor sample with standard hydrochloric acid to a methyl orange end point.

Odorous organic gases were analyzed by gas chromatography according to procedures developed by Adams^{33, 34, 35, 36} for the National Council for Stream Improvement. The gases are concentrated by freezing them out on silica gel at -78.5°C . Moisture is removed prior to freeze-out by passing the gas through an ice water condenser and a Drierite adsorption trap (see Figure 7). The sample is desorbed from the silica gel at 100°C and analyzed by gas chromatography (see Appendix I).

Detailed particulars covering the analytical procedures previously described are presented in Appendix I beginning on page 107.

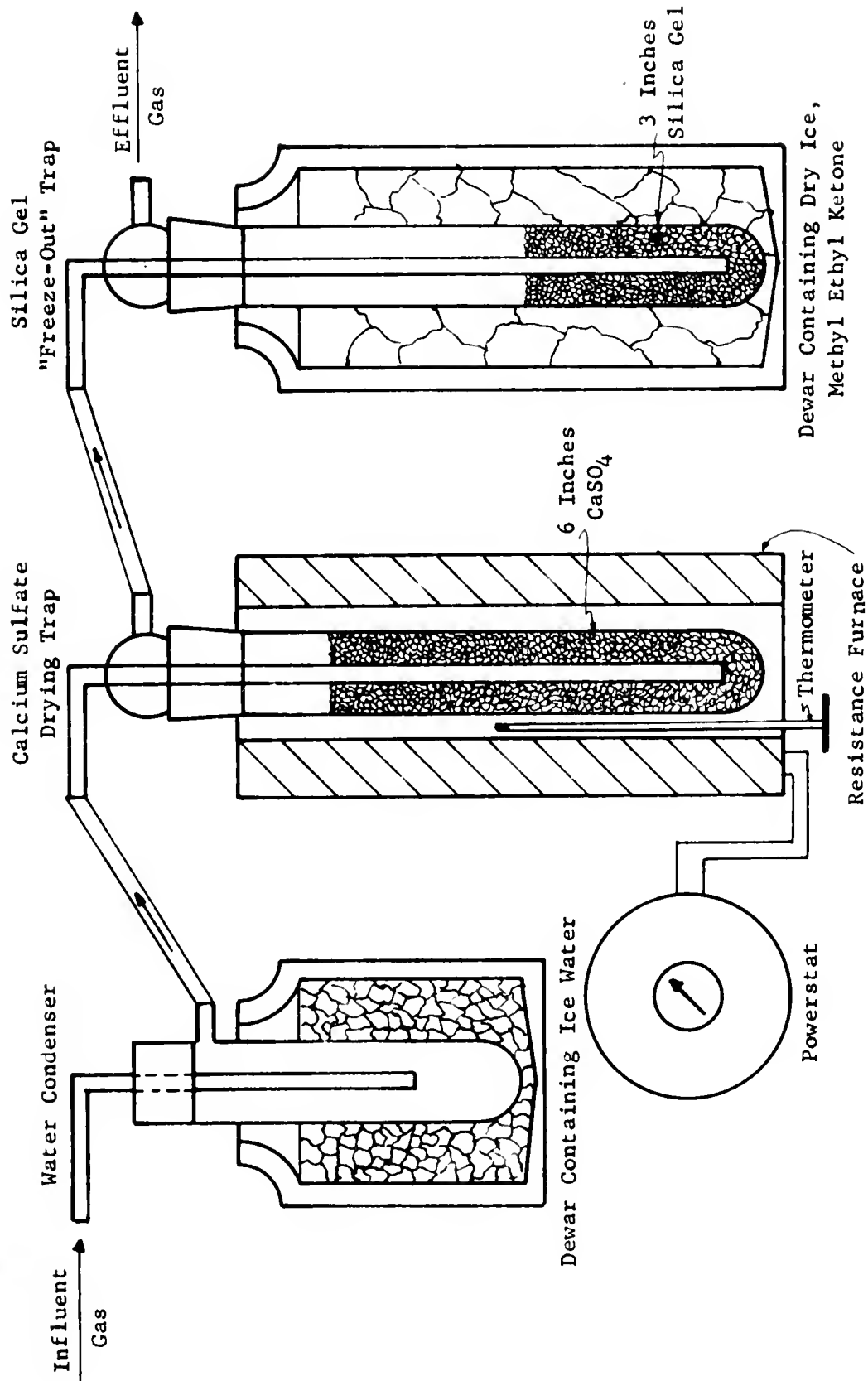


Fig. 7.-Sampling equipment for concentrating and collecting odorous gases.

CHAPTER VI

DISCUSSION OF RESULTS

Black liquor oxidation was investigated at different conditions to determine the relative importance of certain variables on the system. In a typical mill black liquor is kept near boiling; hence the temperature range of practical interest is 60°C to 90°C. Oxidation was conducted at atmospheric pressure using pure oxygen. As the temperature increased, thus increasing the water vapor pressure, the oxygen partial pressure was in turn decreased. Therefore, temperature and oxygen pressure are not independent but are dependent variables which vary inversely.

The contact surface, quantity of agitation, and other contact variables have an influence on the oxidation rate. When the temperature and oxygen pressure were studied, the contact variables were held fixed. When the method of contact was investigated, the temperature and oxygen pressure were held constant. In this manner the effect of temperature, oxygen pressure, and method of contact on the underlying chemistry of the system was determined.

The use of ozone to eliminate odor has been suggested by persons experienced in the field of sanitary engineering.³⁷ Ozonating pulp mill odors and accelerating black liquor oxidation with ozone have been evaluated.

Chemistry of Black Liquor Oxidation

The initial phase of this investigation dealt with the inorganic reactions that transpire during oxidation and the effect of temperature and oxygen pressure on the products formed. Analysis conducted according to standard procedures (TAPPI T625m-48) showed considerable concentrations of sulfide, thiosulfate, and sulfate but not sulfite present. Other analyses conducted on the unoxidized black liquor included total solids, specific gravity, percentage inorganic and organic matter, hydrogen ion concentration (pH), hydroxide, and carbonate. Once a clear picture of the major mineral constituents of black liquor was obtained, oxidation tests were conducted and the changes in the inorganic compounds observed.

Initial tests were conducted at 75°C which was the median condition in the temperature range (60° to 90°C) under consideration. Samples were withdrawn at 10- to 15-minute intervals during static oxidation and analyzed for sulfide, thiosulfate, sulfite, and sulfate. The hydrogen ion, hydroxide, and carbonate concentrations were determined before and after oxidation. Chemical changes produced by oxidation are shown in Table 4 and Figure 8.

No change in pH, hydroxide, or carbonate was found to occur with oxidation. The sulfur compounds, however, were affected by oxidation (Figure 8). Thiosulfate was formed by the oxidation of sulfide but the sulfate content remained unchanged. Apparently the conditions studied were not severe enough to drive sulfide all the way to its sulfate form. No sulfite was detected before, during, or after oxidation and it was suspected that thiosulfate was the highest common oxidation state of sulfur formed under normal conditions.

TABLE 4

EFFECT OF OXIDATION ON HYDROGEN ION, HYDROXIDE, AND
CARBONATE CONCENTRATIONS IN BLACK LIQUOR

Static Oxidation for 180 Minutes With Pure Oxygen at 75°C			
Material	Concentration		Difference
	Before Oxidation	After Oxidation	
Hydrogen Ion (pH)	11.8	11.8	0
Hydroxide as Grams per Liter NaOH	11.0	10.9	-0.1
Carbonate as Grams per Liter Na ₂ CO ₃	11.7	11.7	0

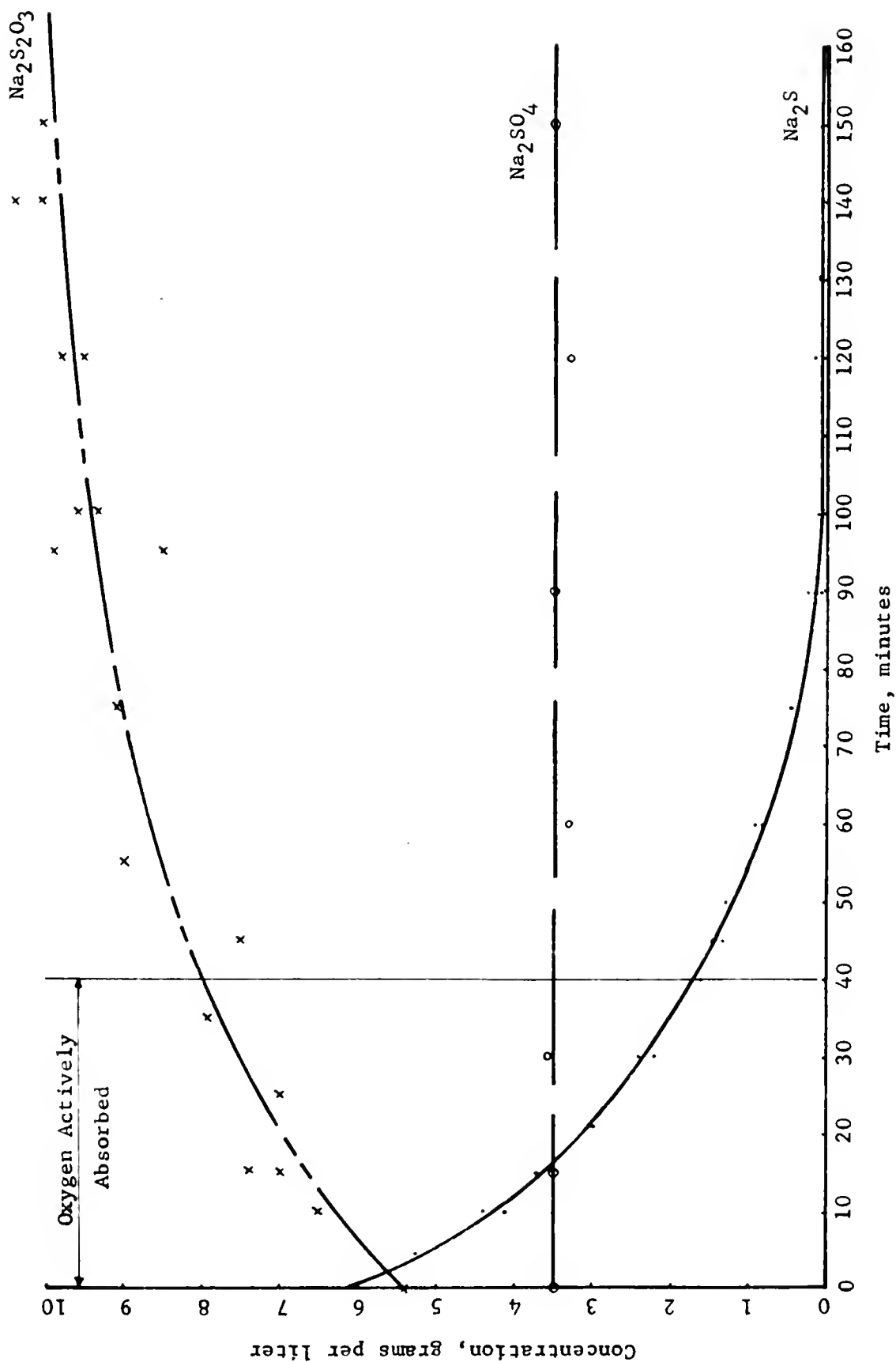


Fig. 8.-Effect of oxidation on the sulfur compounds in black liquor.
Static oxidation with pure oxygen at 75°C.

A material balance was calculated to determine whether or not all the sulfur initially present was accounted for in oxidized form after stabilization. Table 5 shows that 25.6 per cent of the sulfide sulfur was not accounted for by the thiosulfate produced. The rate of formation of the unknown compound or compounds was calculated by difference and plotted in Figure 9.

The question of identifying these unknown compounds and establishing routine methods of analysis was next approached. The situation was complicated by the fact that no fewer than five stable oxidation states are known to exist between sulfide sulfur with an oxidation number of -2 and thiosulfate sulfur with an oxidation number of +2. If the more oxidized forms than thiosulfate are considered and, excluding the sulfate and sulfite which have been accounted for, the matter is further complicated by the persulfates, hyposulfate, and dithionate.

Since no sulfite or sulfate was produced, it seemed likely that at least some of the unaccounted for sulfur was present in oxidation states between the sulfide and thiosulfate form. The stable oxidation states in this region fall into two categories, elemental sulfur and the polysulfides. Elemental sulfur is insoluble in aqueous solution although it decomposes slowly under alkaline conditions. Some visual evidence of sulfur, if present, should be detectable in the oxidized black liquor. At 75°C no sulfur formation was observed. Therefore it seemed unlikely that sulfur was a major stable product of oxidation. The polysulfides are stable in alkaline solution and are a possible decomposition product of sulfide.

TABLE 5
MATERIAL BALANCE OF KNOWN AND UNKNOWN SULFUR COMPOUNDS

Static Oxidation for 180 Minutes With Pure Oxygen at 75° C			
Sulfide Initially Present in Fresh Liquor Expressed as Moles per Liter Sulfur	Thiosulfate Formed by Oxidation Expressed as Moles per Liter Sulfur	Unaccounted for Compounds Expressed as Moles per Liter Sulfur	Unaccounted for Compounds Expressed as Mole Percentage of Initial Sulfide Sulfur
0.079	0.058	0.021	25.6

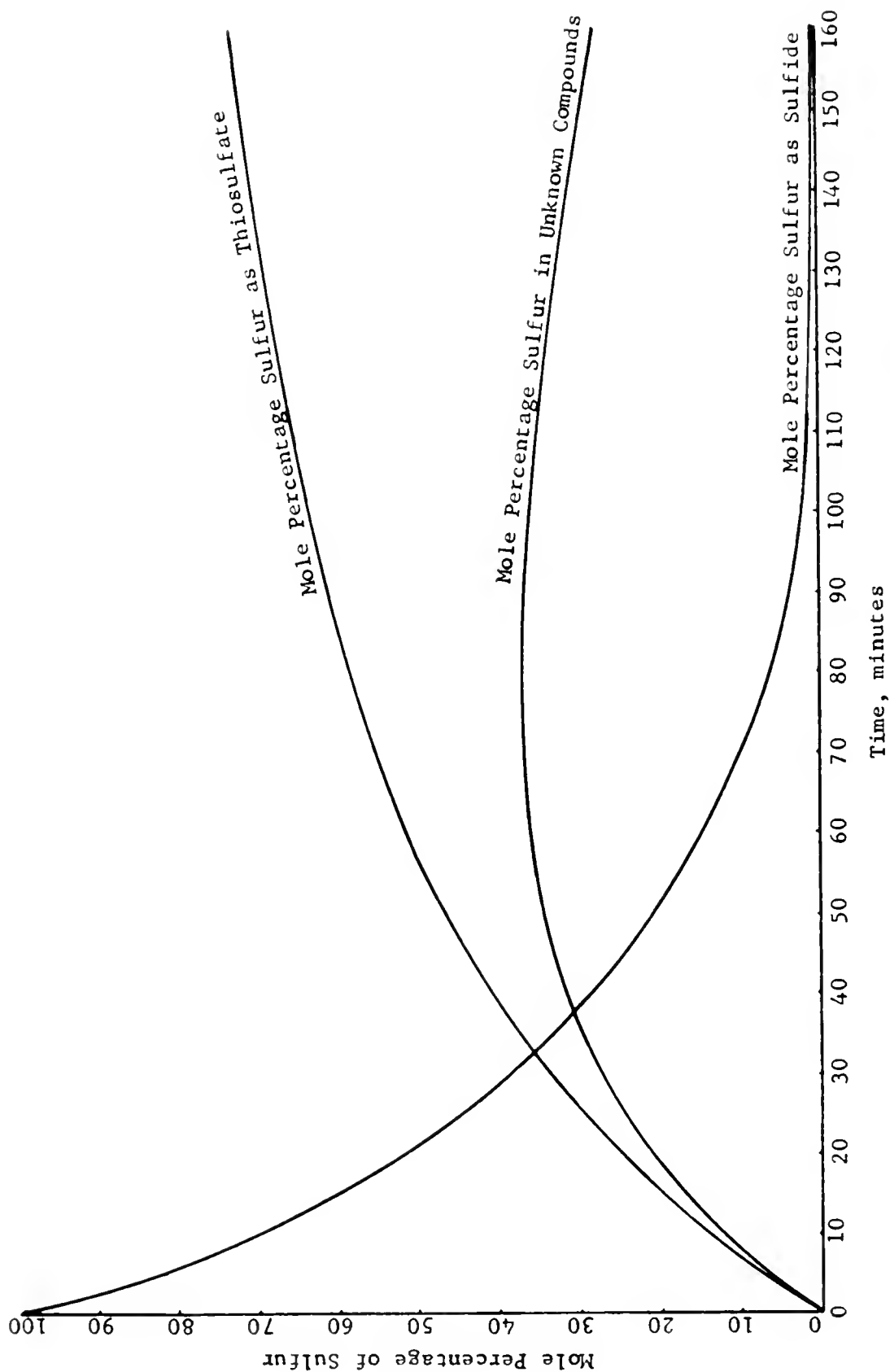


Fig. 9.-Rate of formation of known and unknown sulfur compounds. Static black liquor oxidation with pure oxygen at 75°C.

Of the polysulfides four stable oxidation forms -- the di, tri, tetra, and penta-sulfide -- are known. Separation of the four forms is difficult and since the disulfide is believed to be the most predominant form, quantitative analysis usually determines total polysulfides and expresses the results as disodium disulfide, Na_2S_2 . Scott's Standard Methods of Chemical Analysis³¹ suggests a quantitative method for sodium polysulfide. Since the analysis is based on the fact that the soluble polysulfides will precipitate sulfur quantitatively in a strongly acid solution, it is not directly applicable to black liquor without elimination of certain interferences. The method was adapted by precipitating the sulfides and lignin in the black liquor with zinc chloride and hydrochloric acid, respectively. Filtering out these precipitates left a fairly pure solution from which polysulfide sulfur could be precipitated by acidification and digestion. The sulfur was collected, dried, and weighed in sintered glass crucibles. To check the purity of the precipitate, several of the crucibles were extracted with carbon disulfide and reweighed. The precipitate was completely soluble in carbon disulfide indicating that the sulfur was relatively free from impurities.

This analysis showed polysulfides were present in both the fresh and the oxidized liquor. Once a second oxidation product was established, the oxidation at 75°C was repeated to determine the changes that occurred in sulfide, thiosulfate, and polysulfide concentrations. At 60°C and 89°C the above mentioned sulfur compounds as well as pH, hydroxide, and carbonate concentrations were determined before and after oxidation. The oxidation of sulfide to polysulfide and thiosulfate is shown in Figure 10, and the sulfur balances over the entire temperature range is presented in Tables 6 and 7.

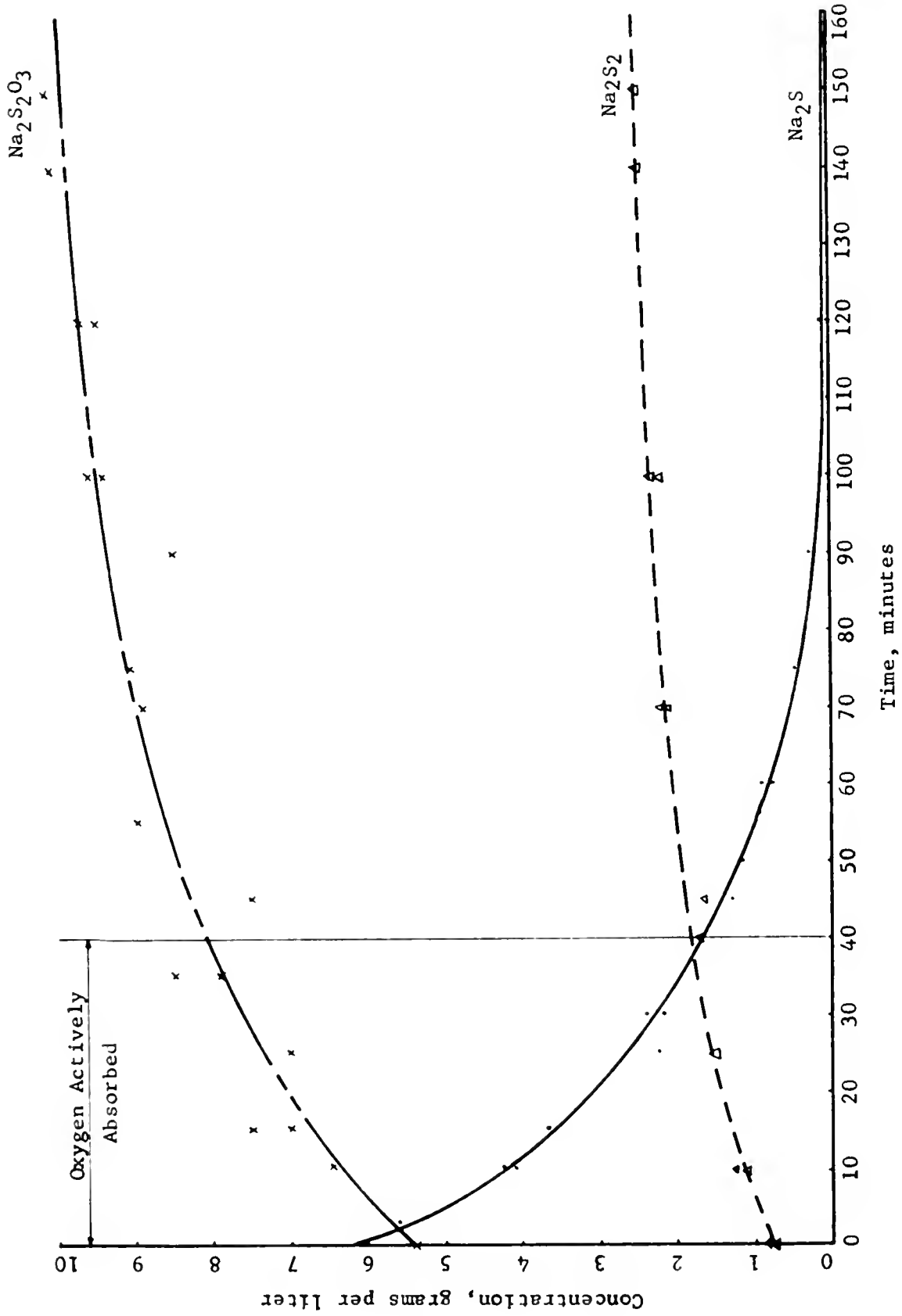


Fig. 10.-The oxidation of sulfide to polysulfide and thiosulfate.
Static black liquor oxidation with pure oxygen at 75°C.

TABLE 6

SULFUR BALANCE BEFORE AND AFTER COMPLETE OXIDATION

Static Oxidation for 180 Minutes With Pure Oxygen							
Temperature °C	Sulfide Expressed as Moles per Liter Sulfur		Polysulfide Expressed as Moles per Liter Sulfur		Thiosulfate Expressed as Moles per Liter Sulfur		Sum
	Before	After	Before	After	Before	After	
60	0.075	0.000	0.014	0.045	0.073	0.120	0.162 0.165
75	0.075	0.000	0.014	0.047	0.069	0.127	0.162 0.174
89	0.078	0.000	0.015	0.048	0.075	0.125	0.168 0.173
							+1.8
							+6.9
							+2.9

Percentage Error

TABLE 7
SULFUR BALANCE DURING COMPLETE OXIDATION

Static Oxidation With Pure Oxygen at 75°C					
Time in Minutes	Sulfide Expressed as Moles per Liter Sulfur	Polysulfide Expressed as Moles per Liter Sulfur	Thiosulfate Expressed as Moles per Liter Sulfur	Sum	Percentage Error
0	0.079	0.014	0.069	0.162	0
30	0.030	0.031	0.096	0.157	-3.1
60	0.011	0.038	0.109	0.158	-2.5
90	0.003	0.042	0.118	0.163	+0.6
120	0.001	0.045	0.122	0.168	+3.7
150	0.000	0.046	0.125	0.171	+5.5
180	0.000	0.047	0.127	0.174	+6.9

Under the conditions studied, the sulfur balance (see Table 6) accounted for all of the sulfide oxidation products in the system with an average error of 3.9 per cent. The sulfur balance calculated at 30-minute intervals throughout oxidation (Table 7) confirmed the fact that no appreciable amounts of unknown inorganic sulfur compounds were formed during any stage of the oxidation. Therefore, it was thought that most of the experimental error was caused by inaccuracies in the thiosulfate analysis. Since the thiosulfate determination tended to produce high results (see Appendix I) and the error of closure was in the same direction, a considerable portion of the error may be attributed to the determination. The remaining differences were attributed to various other forms of experimental error.

It is entirely possible, of course, that compounds of sulfur other than polysulfide and thiosulfate were formed by oxidation. These compounds, however, were not formed in significant concentrations from the inorganic hydrous sulfide. Thus, these trace compounds were of little practical importance. Because all the sulfur was accounted for within reasonable limits of experimental error, the presence of trace compounds other than elemental sulfur was not determined.

The matter of trace quantities of sulfur present in the black liquor was investigated for two distinct reasons. The first was the theoretical consideration that elemental sulfur should not be stable in a strongly alkaline solution. The second reason was that the precipitation of sulfur during oxidation was reported by a previous worker in the field.⁸

To determine the conditions conducive to sulfur formation, samples of black liquor were oxidized in the reaction chamber (Figure 5) at 89°C, 75°C, 60°C, 45°C, and 30°C. No sulfur was formed at 89°C and 75°C. Traces of sulfur were noticed at 60°C while at the two lower temperatures a definite scum formed. The sulfur was very finely divided and continued stirring led to agglomeration. To determine the order of magnitude of the precipitated sulfur, 100-milliliter samples were placed in a gas impinger and oxidized with oxygen. When analysis indicated that the sodium sulfide content had dropped to 0.05 grams per liter or less, the samples were filtered through sintered glass crucibles and thoroughly washed. The precipitate was dried at 75°C and the weight of sulfur expressed as grams per liter (see Table 8). The concentration of sulfur precipitated during oxidation was in the range of 0.004 to 0.005 grams per liter. This meant that the amount of sulfur formed was about one thousand times smaller than the polysulfide and the thiosulfate formed. Since this sulfur formation was negligible compared to other reactions, it is easy to see why a major discrepancy did not appear in the sulfur balance in Table 6.

To investigate the stability of the precipitated sulfur, a portion was collected and washed free of black liquor. Examination under a microscope showed the precipitate to be comprised of irregular bunches of tiny spherical sulfur droplets. These droplets, which were insoluble in carbon disulfide, exhibited no crystalline structure under 1455X magnification. When the precipitated sulfur was aged about four hours at room temperature, the drops began to grow into irregular crystals. At room temperature (25°C) about 3-days storage in aqueous solution was

TABLE 8

CONCENTRATION OF AMORPHOUS SULFUR FORMED

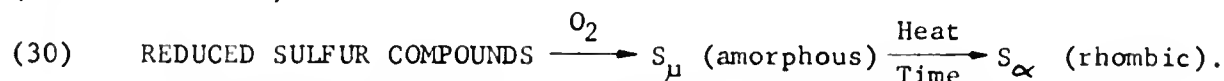
BY BLACK LIQUOR OXIDATION

Oxidation in Gas Impinger With Oxygen
Sulfur Concentrations Expressed as Grams per Liter Sulfur

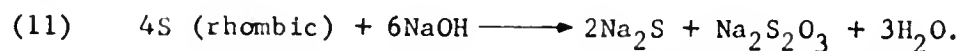
Temperature °C		
30	45	60
0.004	0.001	0.007
0.006	0.006	0.004
<u>0.003</u>	<u>0.005</u>	<u>0.005</u>
Average 0.004	Average 0.004	Average 0.005

required to complete this crystallization. The resulting crystals were completely soluble in carbon disulfide. Photomicrographs of this metamorphosis from amorphous droplets to rhombic crystals are shown in Plates 2 through 4. The comparison between the crystal structure of the aged droplets and the commercial-grade elemental sulfur can be seen in Plates 4 and 5. From the 0.5- to 1.0-micron particle size it appears that the sulfur was precipitated very slowly, possibly as a decomposition product of an organic complex.

The trace of amorphous sulfur will eventually disappear if aged long enough in the oxidized black liquor. Experimentation showed it was apparently immaterial whether the liquor was stored aerobically or anaerobically. The controlling factor was storage temperature. Above 60°C the re-resolution of sulfur was definitely accelerated. The probable reason for this disappearance was that the amorphous or μ sulfur crystallized into rhombic or α sulfur which is unstable in alkaline solution (see reaction 30).

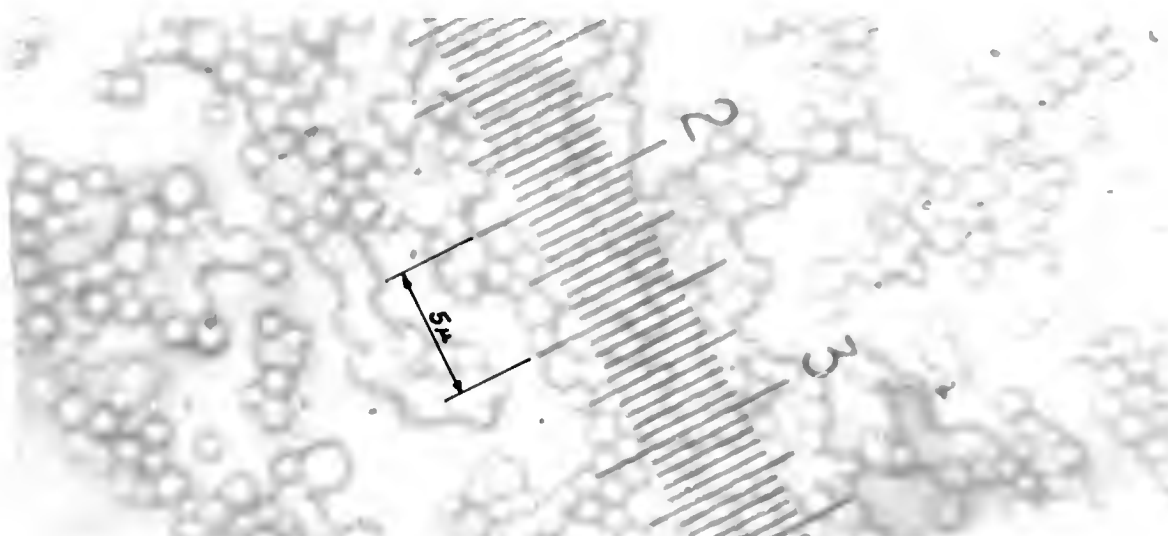


The crystalline rhombic sulfur will decompose probably according to reaction 11.

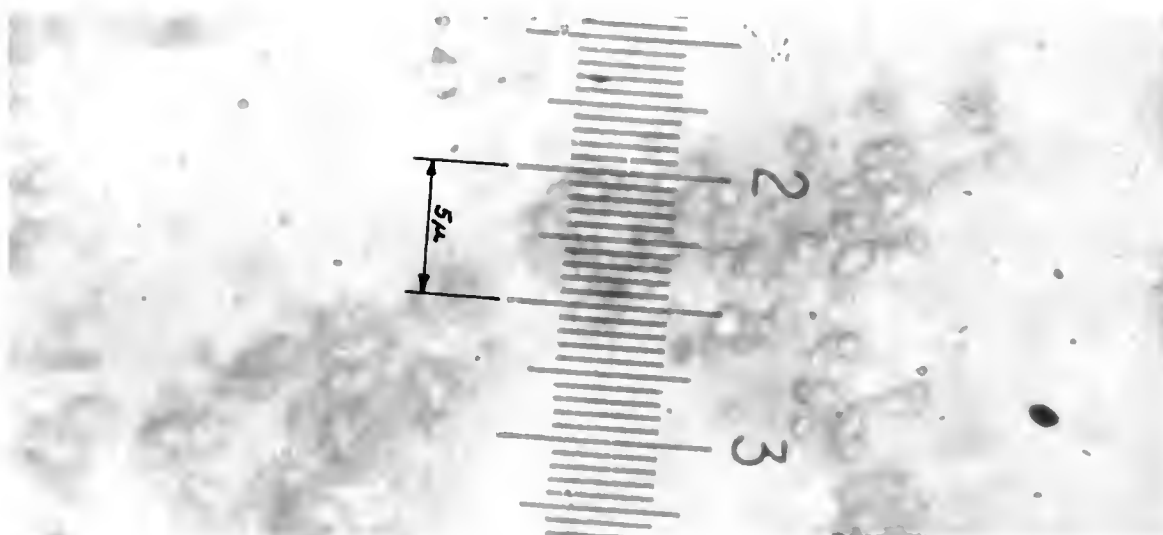


Under aerobic conditions the sodium sulfide formed will in turn be oxidized to thiosulfate and polysulfide.

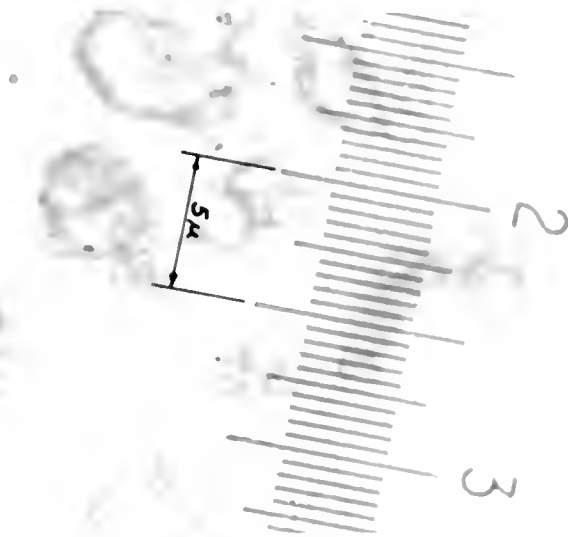
On the basis of the previous discussion and the data presented in Tables 4 through 8, and Figures 8 through 10, certain generalizations can be made regarding the reactions that take place during oxidation.



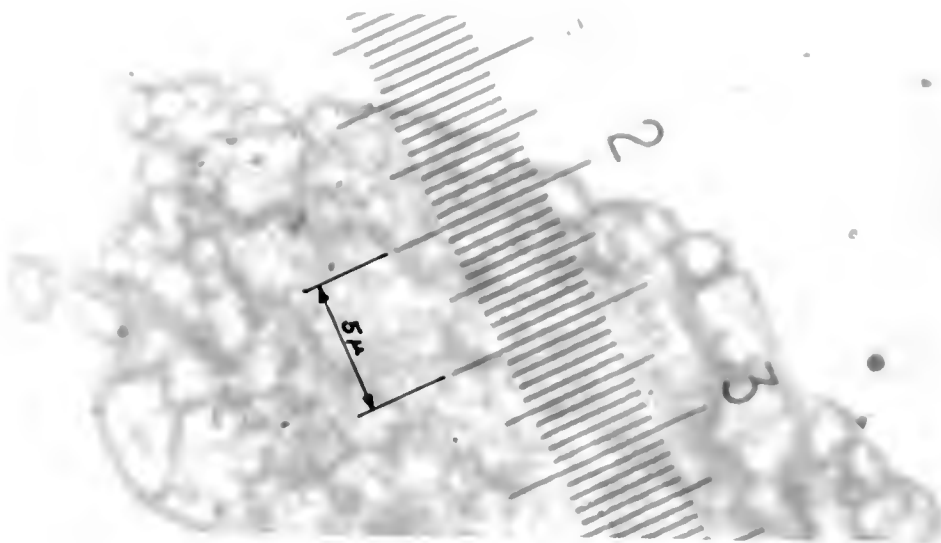
Pl. 2.-Photomicrograph of freshly precipitated amorphous sulfur droplets.



Pl. 3.-Photomicrograph of precipitated sulfur after aging four hours at 25°C.



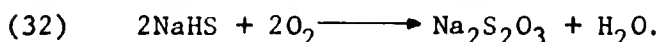
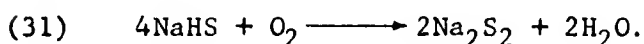
Pl. 4.-Photomicrograph of precipitated sulfur after aging three days at 25°C.



Pl. 5.-Photomicrograph of commercial grade elemental sulfur.

The sulfide in black liquor was completely hydrolyzed and present in the form of hydrosulfide ion, HS^- . If this was not true and the sulfide ion, S^{2-} , was present, an increase in hydroxide concentration according to reaction 1 would occur during oxidation. Since no such increase was found (Table 4), the conclusion was drawn that all the sodium sulfide was hydrolyzed to sodium hydrosulfide and sodium hydroxide during the digestion period (see reaction 4).

On the basis of the curves in Figure 8 and the sulfur balance in Table 6, the premise that sulfate ion was a product of black liquor oxidation cannot be verified. These findings are in direct contradiction to the work of Collins (Table 2). Collins' work was conducted in an air bubbler at 82°C , and it is difficult to explain how he could have oxidized some of the soluble sulfide to sulfate. These results may be accounted for by differences in the black liquor or possibly by different methods of analysis. It is believed, therefore, that equations 31 and 32 describe the primary inorganic reactions that take place during black liquor oxidation.



It is also believed that reactions 31 and 32 more precisely describe the fate of the dissolved sulfide than the unconfirmed reactions 1 and 10. A relatively minor reaction that also occurs during oxidation is the formation of amorphous elemental sulfur from the liquor.



The oxidation states of sulfur as disodium disulfide and sodium thiosulfate are -1 and +2, respectively. It was initially suspected that

in the absence of any data to the contrary, thiosulfate might be an oxidation product of the more reduced polysulfide form. The shapes of the thiosulfate and polysulfide curves in Figure 10 indicate, however, that these two products were formed simultaneously rather than consecutively. The flat slope of the polysulfide curve and the lack of a maximum point showed that the thiosulfate was not an oxidation product of polysulfide. Therefore, oxidation reactions 31 and 32 were parallel rather than consecutive as might be suspected. The latter reaction proceeded at a faster velocity than the former and produced a greater concentration of oxidation products from the black liquor [hydrosulfide].

Optimum conditions of temperature and oxygen pressure are important considerations in black liquor oxidation. In a static oxygen contact system (Figure 5) at a pressure of 1.0 atmosphere, a rise in temperature from 60°C to 89°C lowered the oxygen tension above the liquor from 0.803 atmospheres to 0.334 atmospheres. These two dependent parameters appeared to have little or no over-all effect on the products of reaction. Table 9 shows the ratio in mole fraction of the thiosulfate to polysulfide produced. The variation in this ratio which averaged 1.60 was small and it was concluded that the oxidation products formed were relatively independent of temperature.

To determine whether or not the method of contact influenced the oxidation products, experiments were performed at 75°C using a dynamic oxygen flow (Figure 6). Tests were also conducted to verify the work of Collins.¹⁶ This was done by oxidizing black liquor at 82°C in an air bubbler. At these experimental conditions large excesses of oxygen and air were provided. Tables 10 and 11 show the change of certain sulfur

TABLE 9

RATIO OF THIOSULFATE TO POLYSULFIDE PRODUCED BY COMPLETE OXIDATION

Static Oxidation for 180 Minutes With Pure Oxygen			
Temperature °C	Thiosulfate Produced Expressed as Moles per Liter $\text{Na}_2\text{S}_2\text{O}_3$	Polysulfide Produced Expressed as Moles per Liter Na_2S_2	Mole Ratio of Thiosulfate to Polysulfide Produced
60	0.0235	0.0155	1.52
75	0.0290	0.0165	1.76
89	0.0250	0.0165	<u>1.52</u>
		Average	1.60

TABLE 10

EFFECT OF PURE-OXYGEN OXIDATION ON THE SULFUR COMPOUNDS IN BLACK LIQUOR

Dynamic Oxidation With a Flow of 450 Milliliters per Minute of Pure Oxygen at 75° C					
Test Number	Time in Minutes	Sulfide Expressed as Grams per Liter Na_2S	Polysulfide Expressed as Grams per Liter Na_2S_2	Thiosulfate Expressed as Grams per Liter $\text{Na}_2\text{S}_2\text{O}_3$	Sulfate Expressed as Grams per Liter Na_2SO_4
1	0	5.70	0.79	4.85	3.14
	126	0.00	2.80	11.20	2.97
2	0	5.52	0.75	5.65	3.05
	120	0.14	2.75	10.25	2.98
3	0	5.60	0.76	5.75	2.96
	120	0.06	2.60	7.70	3.24

TABLE 11
EFFECT OF AIR OXIDATION ON THE SULFUR COMPOUNDS IN BLACK LIQUOR

Dynamic Oxidation With a Flow of 300 Milliliters per Minute of Air in An Impingement Type Bubbler at 82°C				
Test Number	Time in Minutes	Sulfide Expressed as Grams per Liter * Na_2S	Sulfate Expressed as Grams per Liter * Na_2SO_4	Sample Volume in Milliliters
1	0	5.80	2.85	125
	60	0.03	2.97	100
2	0	5.80	2.72	125
	60	0.02	2.86	100
3	0	5.75	3.17	125
	60	0.39	3.63	100

* Corrected for volume loss by evaporation; concentrations based on original volume, containing 14.8 per cent total solids.

compounds upon oxidation. Even with great excesses of oxidizing agent sulfate was not a product of oxidation. It was concluded that in the temperature range considered the rate of oxidation may depend on the method of contact but the ultimate oxidation products formed do not. Miscellaneous other studies showed that application of 1450 parts per million (0.1450 per cent) of ozone was insufficient to oxidize any of the reduced sulfur compounds to sulfate.

Reversibility of the Oxidation Reactions

When in contact with oxygen at elevated temperatures, the sodium hydrosulfide in black liquor spontaneously oxidizes to disodium disulfide and sodium thiosulfate. The degree to which these reactions are reversible when the oxygen is removed was investigated. This reversibility may create odor problems since in practice the black liquor may be stored anaerobically for a length of time after oxidation and before evaporation. If volatile sulfur compounds are regenerated, some of the effect of oxidation will be lost. Murray⁸ reported that sulfide was regenerated when black liquor was stored anaerobically, but he did not explore this observation or attempt to explain it. This regeneration can be explained if reactions 31 and 32 are reversible.

To test this hypothesis, samples of partially oxidized liquor were withdrawn periodically from the oxidizing chamber, analyzed for sulfide, polysulfide, and thiosulfate, and then stored anaerobically at 75°C for 12 hours. At the end of that period the samples were again analyzed for sulfide, polysulfide, and thiosulfate, and the results reported in Table 12. From these data it was concluded that the

TABLE 12

REVERSION OF POLYSULFIDE AND THIOSULFATE UPON ANAEROBIC STORAGE

Static Oxidation With Pure Oxygen at 75°C Anaerobic Storage at 75°C						
Time in Hours	Sulfide Expressed as Grams per Liter Na_2S	Change	Polysulfide Expressed as Grams per Liter Na_2S_2	Change	Thiosulfate Expressed as Grams per Liter $\text{Na}_2\text{S}_2\text{O}_3$	Change
0	1.20	+1.30	1.57	+0.56	8.20	-1.35
12	2.50		2.13		6.85	
0	0.32	+0.62	2.73	-0.01	9.90	-0.65
12	0.94		2.72		9.25	
0	1.25	+1.56	1.14	+0.11	8.10	-0.55
12	2.81		1.25		7.55	
0	3.45	+0.40	1.48	-0.04	7.25	-0.65
12	3.85		1.44		6.60	
0	0.00	+0.03	3.01	+0.29	12.20	-0.20
12	0.03		3.30		12.00	

regeneration of the sulfide is due mainly to the reduction of some of the thiosulfate while the polysulfide formed is relatively stable. The more completely oxidized the black liquor was, the more irreversible was the sodium thiosulfate reaction. Therefore, the oxidation of hydrosulfide (reaction 32) to thiosulfate is partially reversible whereas the oxidation to polysulfide is not.

A more detailed picture of the regeneration is shown in Table 13 and Figure 11. The solid line in Figure 11 shows the rate of oxidation of black liquor at 75°C using a static oxygen system. The dotted curve shows the hydrosulfide concentration if oxidation were stopped at that point and liquor stored anaerobically at 75°C for 12 hours. The reactions involved were much more reversible in the early stages of oxidation when the system was still actively absorbing oxygen. After the oxygen transfer ceased, the hydrosulfide regenerability of the liquor dropped sharply. This would seem to indicate that one mechanism of reaction predominated early in the oxidation while a different mechanism controlled during the final stages. The average degree of regeneration to be expected with this particular liquor at various stages of oxidation is shown in Table 14. To prevent less than 10 per cent regeneration after 12 hours of storage, 80 per cent or more of the black liquor hydrosulfide had to be oxidized. This pointed up the importance of evaporating the liquor immediately after aeration to derive the fullest benefits of oxidation. Regeneration was not pronounced in samples stored anaerobically at room temperature.

TABLE 13

REGENERATION OF SULFIDE UPON ANAEROBIC STORAGE

Static Oxidation With Pure Oxygen at 75°C Anaerobic Storage for 12 Hours at 75°C		
Initial Sulfide Concentration Expressed as Grams per Liter Na ₂ S	Final Sulfide Concentration Expressed as Grams per Liter Na ₂ S	Percentage Sulfide Regeneration Based on Initial Concentration of 6.1 Grams per Liter Na ₂ S
6.10	7.05	+15.6
5.95	6.65	+11.5
5.42	6.99	+25.8
5.31	6.59	+21.0
4.52	6.71	+33.8
3.83	5.11	+37.4
3.71	5.57	+30.5
3.45	3.85	+ 6.5
2.50	3.43	+14.9
2.26	4.10	+30.2
2.03	3.20	+19.2
1.79	2.18	+ 6.1
0.98	1.99	+15.8
0.60	0.89	+ 4.8
0.32	0.94	+10.2
0.13	0.40	+ 4.4
0.12	0.38	+ 4.1
0.00	0.03	+ 0.5

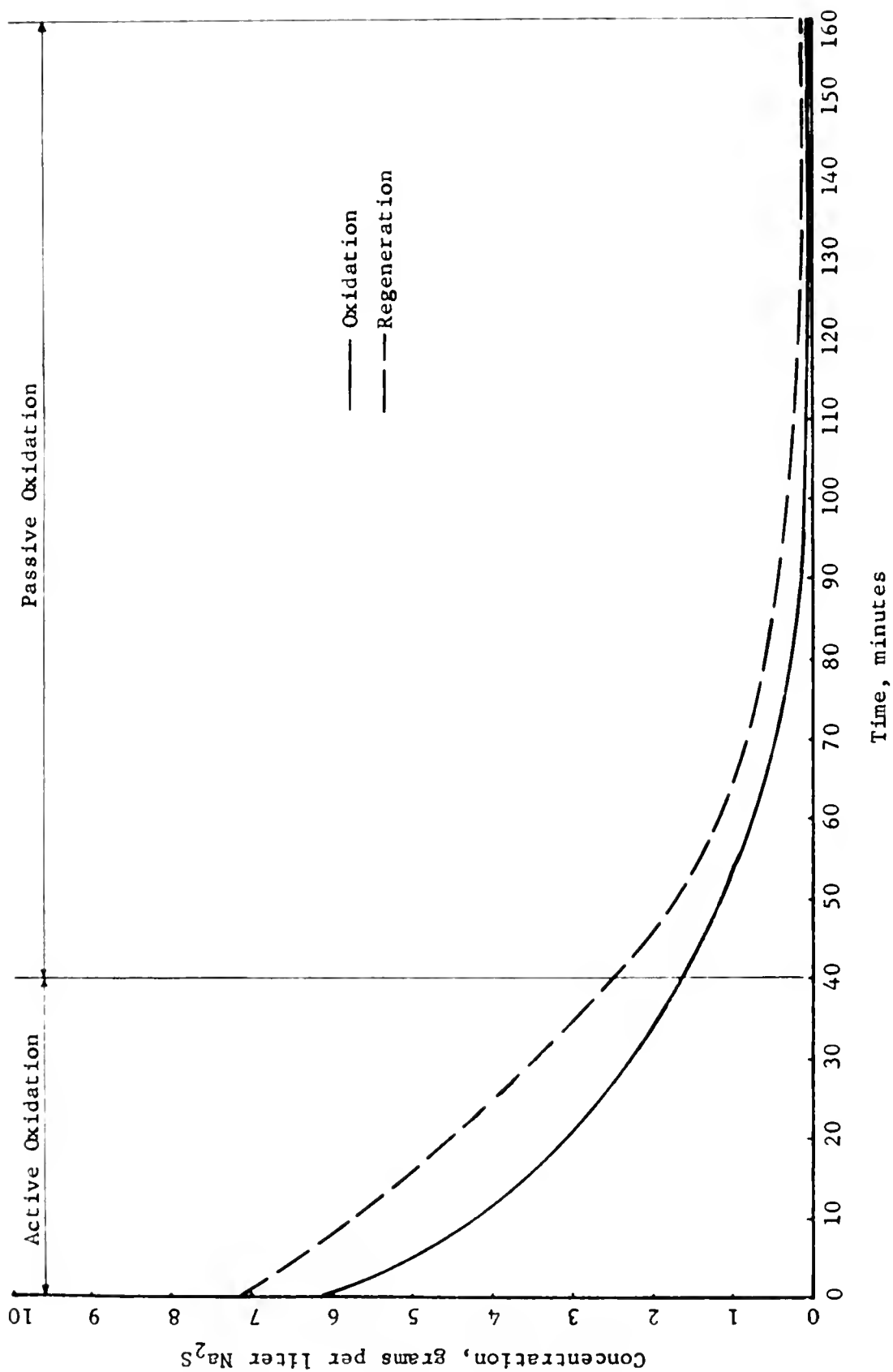


Fig. 11.-Sulfide oxidation and regeneration in black liquor. Static oxidation with pure oxygen at 75°C and 12-hour anaerobic regeneration at 75°C .

TABLE 14

PERCENTAGE REGENERATION OF SULFIDE UPON ANAEROBIC STORAGE

Static Oxidation With Pure Oxygen at 75°C
 Anaerobic Storage for 12 Hours at 75°C
 Based on Curve in Figure 12

Percentage Sulfide Oxidized Based on Initial Concentration of 6.1 Grams per Liter Na ₂ S	Percentage Sulfide Regenerated After 12 Hour Storage at 75°C Based on Initial Concentration of 6.1 Grams per Liter Na ₂ S	Total Percentage Sulfide Present After Regeneration Based on Initial Concentration of 6.1 Grams per Liter Na ₂ S
0	16	116
20	24	104
40	24	84
60	21	61
80	9	29
90	7	17

Oxidation Kinetics

For effective oxidation sufficient quantities of oxygen or air must be brought into intimate contact with the black liquor. Wright⁷ found that infinite contact area did not produce an instantaneous reaction, and he proposed that nothing is gained by increasing the area past a certain point. Assuming that adequate gas-liquid contact can be provided on a mill scale, the reaction kinetics and stoichiometric oxygen requirements become the paramount considerations. In the studies conducted by the author on the kinetics of oxidation, the effect of gas-liquid contact was not eliminated but merely held at a fixed value. This was achieved by holding the stirring rate and gas feed constant. By varying the temperature and hence the oxygen pressure within the system, their effect on the reaction rate could be evaluated. Although it would be difficult to extrapolate the reaction kinetics to actual plant design criteria, comparison of these data at different physical conditions showed the relative importance of the controlling parameters. Once these parameters are evaluated, the gathering of design data for an actual installation is greatly simplified.

The first step was to determine the effect of temperature on oxidation of the dissolved sulfide. Experimental temperatures of 60°C, 75°C, and 89°C were investigated to determine the optimum reaction temperature. A comparison of oxidation at these three temperatures is shown in Figure 12.

When the semi-empirical equation 29, $dC/dt = K (C + bP)$ was fitted to the curves in Figure 12, some quantitative comparisons can be made about the relationship between temperature, reaction rate, and

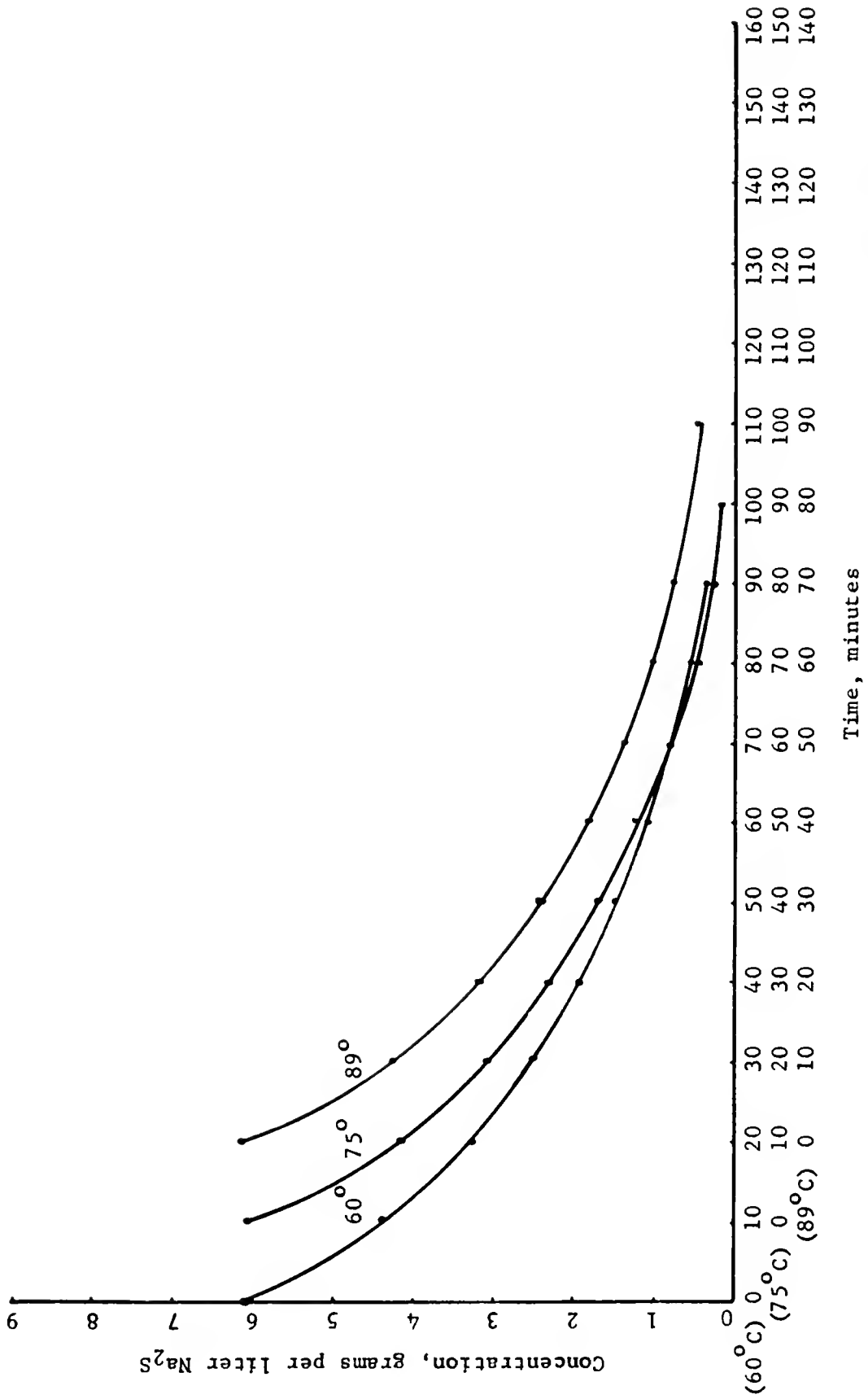


Fig. 12.-The kinetics of sulfide oxidation in Kraft black liquor. Static oxidation with pure oxygen at 75°C.

oxygen absorption. The details of determining the reaction constants K and b in the Appendix II.

A tabulation of the velocity and absorption constants K and b is presented in Table 15. If the oxidation is a true first-order reaction, oxygen absorption will not affect the rate and constant b will be zero. Similarly, if oxidation is independent of the sulfide concentration, the reaction will be of zero order depending solely on the factor K (bP). As can be seen from Table 15, the static system with very low values of bP is very nearly a first-order reaction. This was especially true at 89°C .

A normal "rule of thumb" in chemical kinetics is that the rate constant is doubled with every 10°C rise in temperature. In the case of black liquor oxidation the velocity constant, K , varied only slightly with temperature. The value of K at 75°C was only 23 per cent higher than the value at 60°C . When the temperature was raised to 89°C , the velocity constant began to drop off. Thus, of the three temperatures tested, the reaction velocity was fastest at 75°C .

In connection with the ozone experiments black liquor was oxidized dynamically at 75°C . The oxidation of soluble hydrosulfide in this dynamic system, both with and without ozone, is shown in Figure 13. Apparently 1450 parts per million (0.1450 per cent) of ozone was insufficient to affect the oxidation of the dissolved sulfide, but the ozone did react with the odoriferous gases above the black liquor. A more thorough treatment of the odor problems involved with black liquor oxidation is discussed later. Equation 21 was fitted to this curve and the reaction constants (Table 15) were compared to those of the static

TABLE 15

KINETICS OF BLACK LIQUOR OXIDATION

Based on Curves in Figures 12 and 13
See Appendix II for Details of Calculation

Type of Oxygen Flow	Temperature °C	Kinetic Constants		
		Velocity Constant, K	Oxygen Absorption Constant, b	Oxygen Absorption Product, bP
Static System	60	-0.0241	0.175	0.140
	75	-0.0312	0.177	0.110
	89	-0.0284	0.029	0.010
Dynamic System 450 ml per Minute	75	-0.0100	5.480	3.400

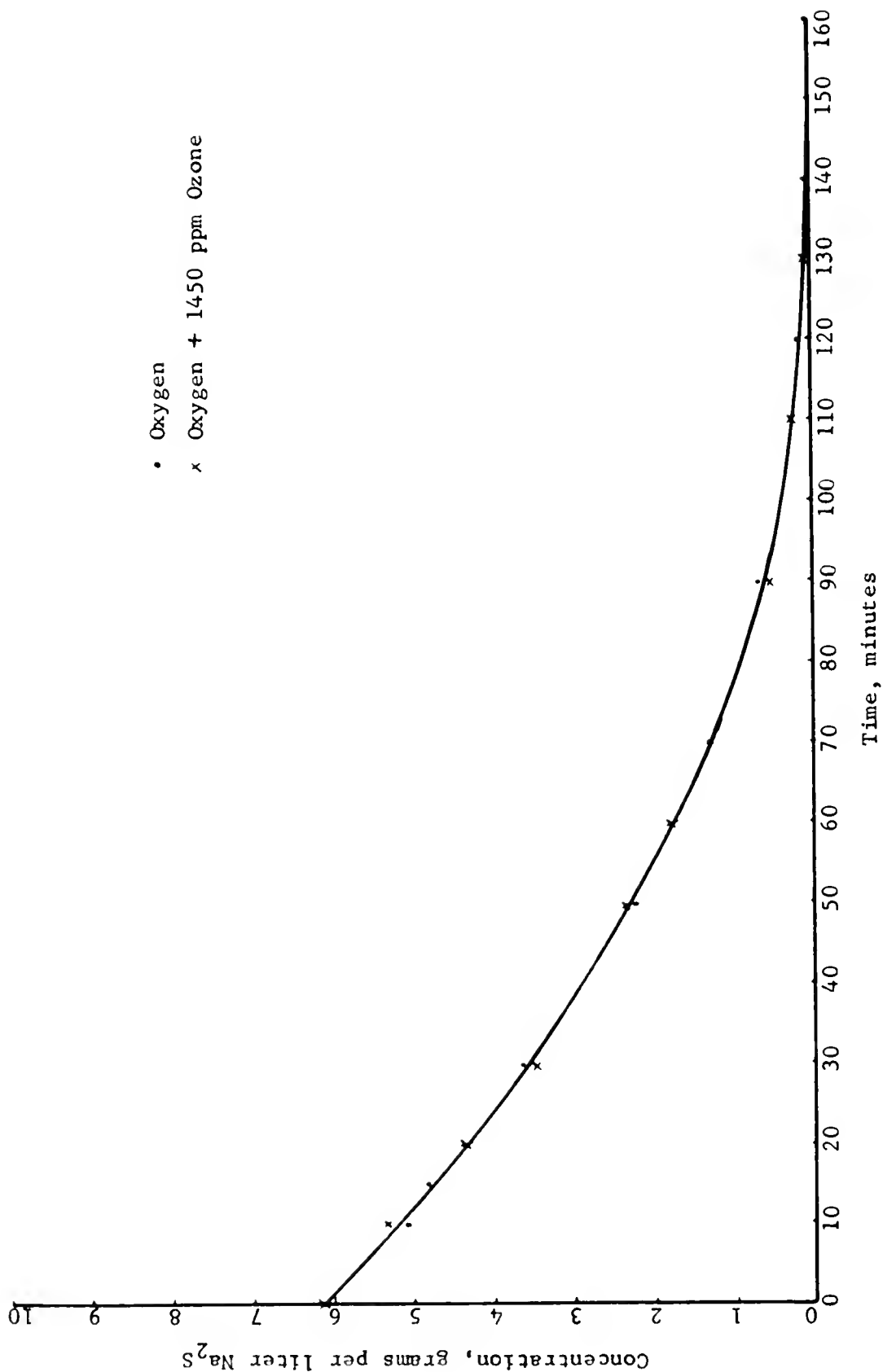


Fig. 13.-The kinetics of sulfide oxidation of Kraft black liquor. Dynamic oxidation at 75°C with pure oxygen and pure oxygen plus ozone.

system. In dynamic oxidation the reaction velocity was only one-third as great as that of the static system. The oxygen absorption factor, however, was increased by a factor of 30. Thus, the over-all reaction was less efficient dynamically than statically and more dependent on the rate of oxygen absorption. Apparently escaping water vapor hindered the oxygen transfer at the gas-liquid interface.

The indirect inferences which may be drawn from the comparison between the two systems should not be overlooked. In both cases the oxidation was conducted under the same conditions except for the method of oxygen feed. The static system was very nearly a first-order reaction, but the dynamic system was significantly influenced by oxygen absorption. This confirms that it was relatively easy for the contact parameters to be the limiting factor in oxidation. In properly designed large-scale equipment, however, contact should be sufficient so that the chemical reaction rate which is a relatively fixed quantity is the limiting factor.

Black Liquor Oxygen Requirements

Additional tests were conducted using a closed static system which enabled the utilized oxygen to be metered. Table 16 shows the variation of oxygen absorbed with changes in temperature. Oxygen absorption was almost doubled as the temperature was raised from 60°C to 89°C. Since the black liquor contained 6.1 grams per liter of sodium sulfide, the theoretical amount required to convert the sulfide to polysulfide and thiosulfate according to reactions 31 and 32 was approximately 1.1 milliliters of oxygen per milliliter of black liquor. At temperatures above 60°C considerably more oxygen was absorbed than

TABLE 16

VOLUME OF OXYGEN ABSORBED BY BLACK LIQUOR DURING OXIDATION

Static Oxidation for 180 Minutes With Pure Oxygen	
Temperature °C	Volume of Oxygen Absorbed by Black Liquor Milliliters of Oxygen* per Milliliter of Black Liquor
60	1.2
75	1.5
89	2.1

*Volume of oxygen corrected to 25°C and 760 millimeters of mercury.

was required to oxidize the sodium sulfide. Thus, as the temperature increased, more and more oxygen was used in side reactions. The percentage of absorbed oxygen used in these side reactions is shown in Table 17. Sixty degrees centigrade was the most desirable temperature of the temperatures tried because most of the oxygen absorbed was utilized in oxidizing the inorganic sulfides. This was not the case at the higher temperatures and at 89°C almost half of the absorbed oxygen was used in extraneous reactions.

Catalysis in the Oxidation of Sodium Sulfide

It has been suggested that the organic matter dissolved in black liquor catalyzes the oxidation of sodium sulfide. This author found that in the range of 60°C to 89°C oxygen absorption practically ceased after 40 to 50 minutes when 1.5 to 1.7 grams per liter of sulfide had yet to be oxidized. This remaining sodium hydrosulfide continued to oxidize with little apparent oxygen absorption. The time lag between oxygen absorption and utilization could be due to chemisorption of oxygen by the liquor.

To test the hypothesis that soluble materials in black liquor catalyze oxidation, a synthetic liquor containing 6.1 grams per liter of sodium sulfide, 5.4 grams per liter of sodium thiosulfate, and 11.0 grams per liter of sodium hydroxide in distilled water was prepared. This liquor contained the same concentration of the principal inorganic compounds found in the black liquor. In a static contact system at 75°C the synthetic liquor oxidized much more slowly (see Figure 14) than the black liquor. Thus it is evident that the black liquor contained

TABLE 17

UTILIZATION OF DISSOLVED OXYGEN

Static Oxidation for 180 Minutes With Pure Oxygen			
Temperature °C	Volume of Oxygen Absorbed Milliliters of Oxygen* per Milliliter of Black Liquor	Volume of Oxygen Required to Oxidize S ⁼ to S ⁻ and S ₂ O ₃ ⁼ Milliliters of Oxygen* per Milliliter of Black Liquor	Volume of Oxygen Excess Expressed as Percentage of Total Volume Absorbed
60	1.2	1.1	8
75	1.5	1.2	14
89	2.1	1.2	45

* Oxygen volume corrected to 25°C and 760 millimeters of mercury.

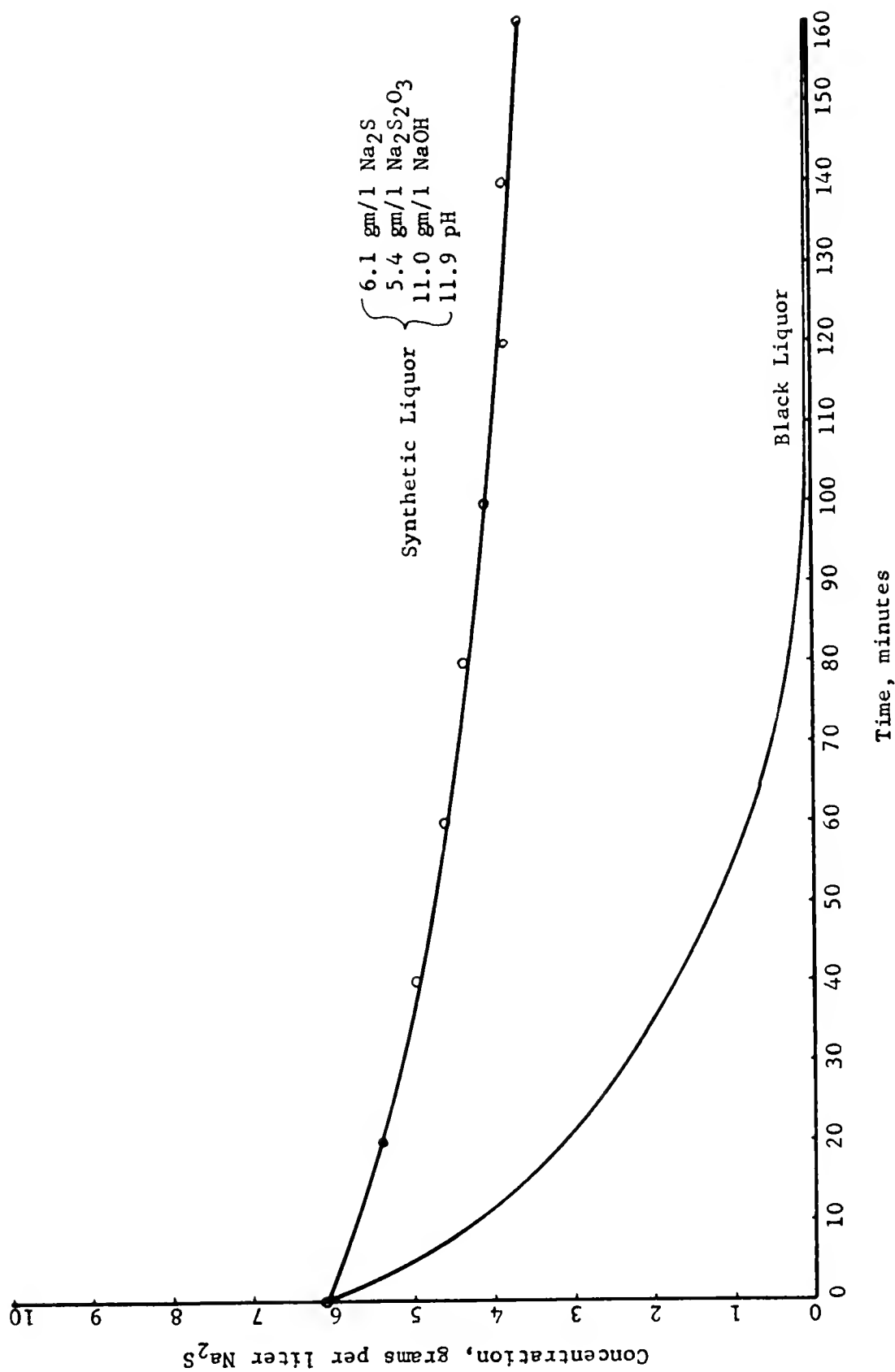


Fig. 14.-Oxidation of sulfide in black liquor and synthetic liquor. Static oxidation with pure oxygen at 75°C .

materials which aided the oxidation. The nature and mechanism of this catalysis is beyond the scope of this dissertation.

Odors Emitted During Oxidation

There was some doubt whether or not black liquor could be oxidized without the emission of odors. The main reason is because of the limited effectiveness of oxygen in oxidizing the mercaptan fraction. In initial tests using dynamic oxygen feed it was noticed that the effluent gases contained the typical Kraft odor. This odor was not present when ozone was added to the influent oxygen stream.

To identify the odorous compounds stripped from the black liquor during dynamic oxidation at 75°C, the off-gases were passed through a -78.5°C cold trap containing silica gel. Moisture was removed from the gas prior to adsorption on the silica gel by passing it through an ice water condenser and a drierite adsorption trap. One-liter samples of black liquor were oxidized to completion (i.e., final Na₂S content of less than 0.05 grams per liter) by excess oxygen supplied at a rate of 450 milliliters per minute. The sulfurous gases collected on the silica gel were desorbed at 100°C according to the procedures developed by Adams^{33, 34, 35} (see Appendix I).

When the mixture was separated and analyzed in the gas chromatograph, methyl mercaptan, ethyl mercaptan, and methyl sulfide were detected in the off-gases. The boiling points of these compounds are 7.6°C, 36.5°C, and 38°C, respectively.

It is reasonable to expect these gases, if present, to be stripped from the liquor when handled at 75°C. No hydrogen sulfide or any of the

long-chain organic sulfides or disulfides were detected in the effluent gases. Since the typical Kraft "rotten vegetable" odor is disagreeable and can be detected in minute quantities (see Table 18), odoriferous organic sulfur compounds will be lost during oxidation unless provision is made to reabsorb or destroy them.

One means of eliminating the odors from oxidation includes reabsorption of the gases by using a concurrent oxidation system. In a concurrent device the effluent gases and the oxidized liquor are moving in the same direction and the liquor has an opportunity to absorb some of the odors in the effluent off-gases. It is unlikely, however, that any of the residual methyl mercaptan with a boiling point of 7.6°C can be contained this way.

This investigation clearly showed that black liquor oxidation is no odor panacea. Although oxidation stabilized the inorganic sulfur and prevented escape of hydrogen sulfide, the single most important odorous gas, the remaining organics still posed a problem. A pure-oxygen system will not have this problem since economics dictate a closed-gas system. If the oxygen is completely absorbed in the black liquor, there will be no off-gases, hence no odors. A pure-oxygen closed system, however, will just transfer the point of emission of the low-boiling mercaptans from the oxidizer to the evaporators. Thus, for the complete elimination of the odors from this portion of the recovery process, the exhaust gases must be treated in some way to destroy the odoriferous mercaptans.

TABLE 18

ODOR THRESHOLDS OF ORGANIC SULFUR COMPOUNDS

FOUND IN BLACK LIQUOR⁴⁵

Compound	Odor Threshold in Milligrams per Liter	Remarks
Methyl Mercaptan CH_3SH	0.00110	Odor of decayed cabbage or onions
Ethyl Mercaptan $\text{C}_2\text{H}_5\text{SH}$	0.00019	Odor of decayed cabbage
Methyl Sulfide $(\text{CH}_3)_2\text{S}$	0.00110	Odor of decayed vegetables

Oxidation of Odorous Gases with Ozone

To determine the feasibility of oxidizing the odors in the exhaust oxygen stream, ozone was added at a steadily increasing rate until no Kraft odor could be detected in the off-gases. This subjective odor analysis was confirmed by collecting the exhaust gas in the "freeze-out" trap and analyzing the gas by chromatography (see Appendix I). When 100 to 150 parts per million of ozone were used, no odorous sulfur gases were detectable by gas chromatography in the exhaust gas. Concentrations above 150 parts per million supplied excess ozone which could be detected in the exhaust.

Ozone is a relatively expensive oxidizing agent. Assuming ozone can be produced commercially at a rate of 2.0 milligrams per coulomb,²⁸ and that commercial power costs \$0.02 per kilowatt-hour, 0.106 pounds of ozone can be produced per kilowatt-hour. The power cost of this ozone will be \$0.189 per pound. This minimum cost of ozone is about four times the cost of chlorine which sells for about \$0.05 per pound wholesale (1961). At a cost of \$0.189 per pound, 150 parts per million of ozone can be produced in a 25°C gas stream at a cost of \$0.0035 per thousand cubic feet of gas treated.

Oxidation of Black Liquor with Pure Oxygen

To be economical on a large scale, pure oxygen must be used in a closed circulation system. Several suggestions for equipment are found in Figures 15, 16, and 17. Assuming an oxygen consumption of 1.2 milliliters of oxygen per milliliter of black liquor, 13.0 pounds of oxygen are required to treat 1000 gallons of black liquor. Assuming an oxygen cost of \$0.09 per pound, oxidation will cost \$1.17 per thousand gallons.

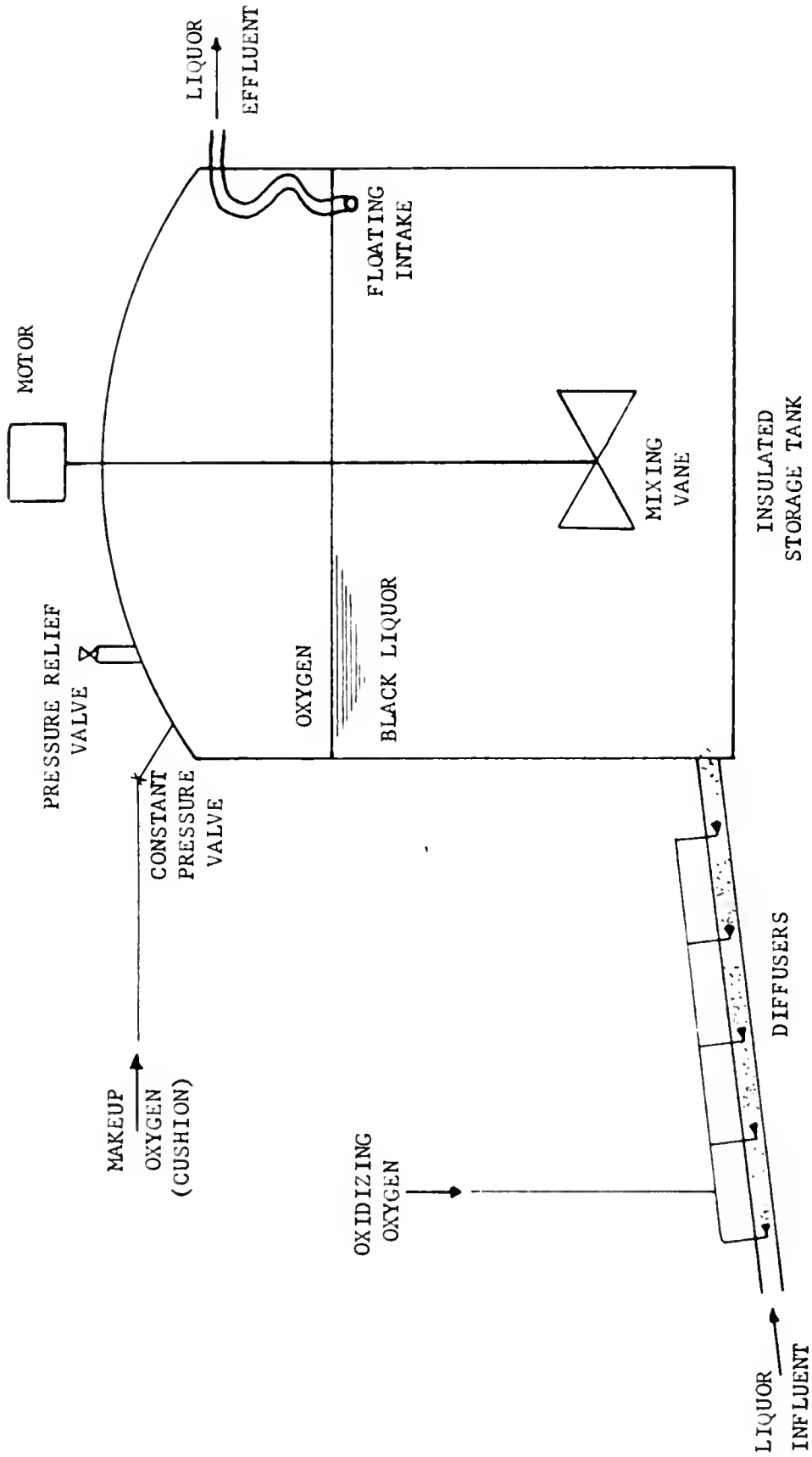


Fig. 15.-Oxidation of black liquor in a storage tank. Suggested equipment requiring little capital investment.

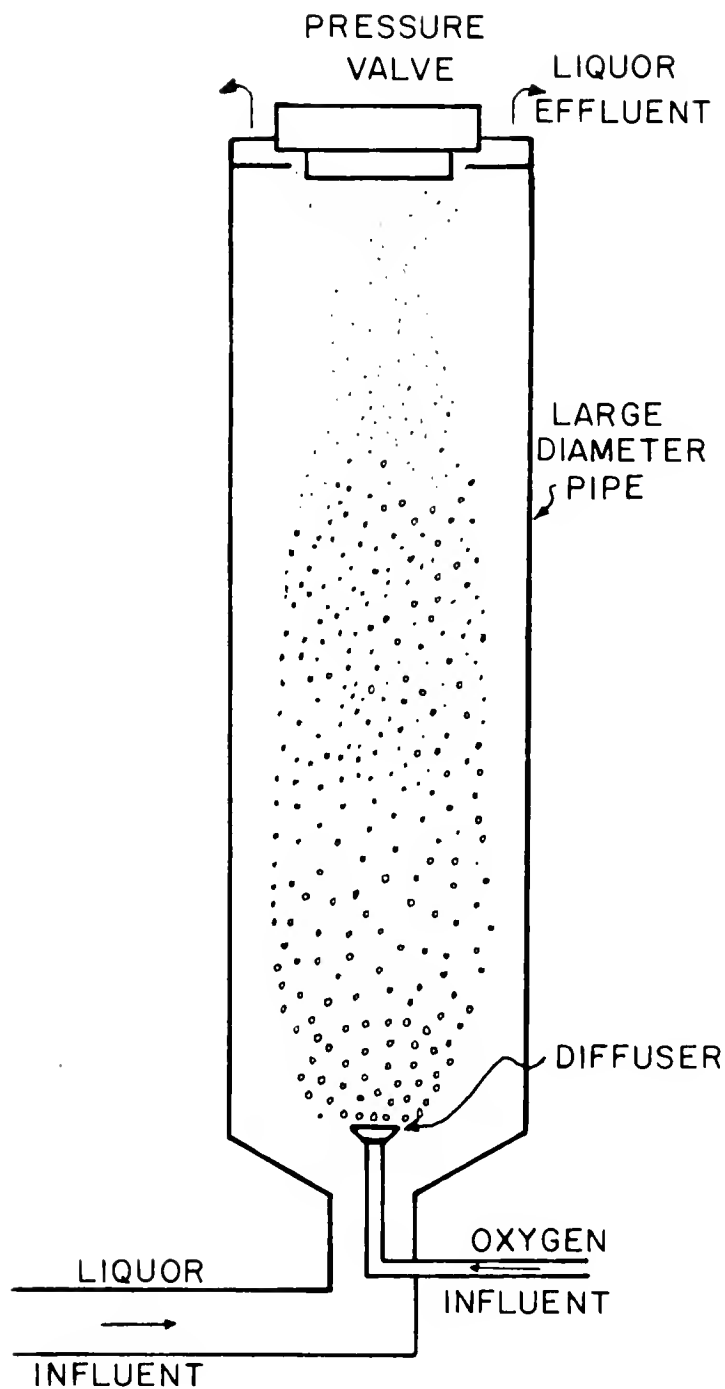


Fig. 16.-Oxidation of black liquor in a pressure-diffuser contactor. Suggested equipment requiring little capital investment.

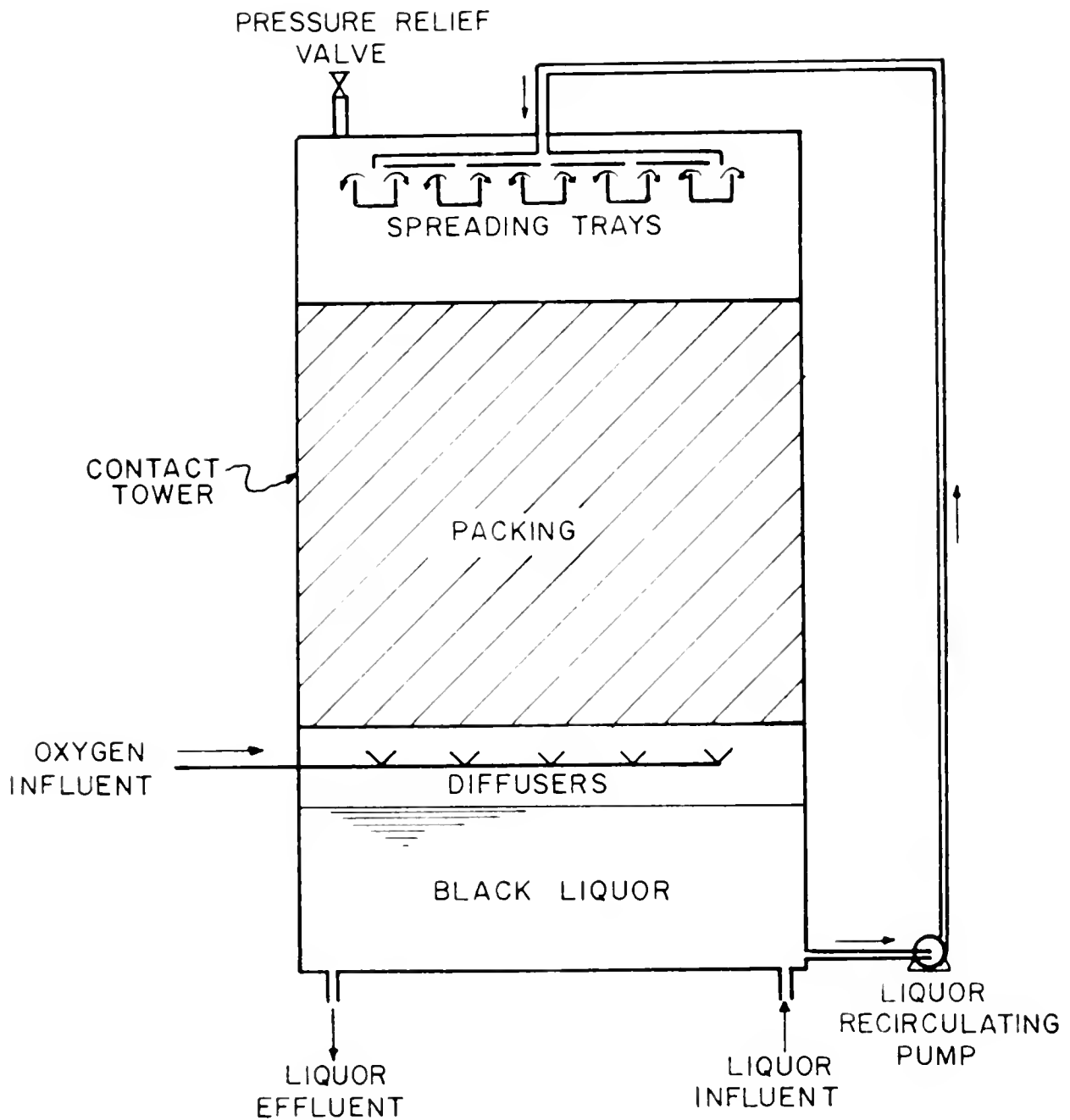


Fig. 17.-Oxidation of black liquor in a recirculating packed tower.

CHAPTER VII

SUMMARY AND CONCLUSIONS

This dissertation was undertaken as a fundamental research project at the University of Florida Air Pollution Laboratory. Black liquor oxidation, a process which reduces air-borne chemical losses, has seen limited use in the Kraft paper industry. Technical difficulties caused by unique characteristics of southern black liquor have impeded the employment of this process in the southeastern United States. In this research an attempt has been made to provide some general criteria which are applicable regardless of location or liquor characteristics. It is hoped that putting black liquor oxidation on a quantitative basis will aid the development of a commercial system applicable to southern Kraft mills.

A southern Kraft black liquor containing 6.1 grams per liter of sodium sulfide was oxidized using pure oxygen. A non-foaming, bench-scale contactor was used and certain physical and chemical parameters varied. The predominant inorganic reactions that occurred were the oxidation of sodium hydrosulfide to sodium polysulfide and sodium thiosulfate. The thiosulfate reaction was slightly reversible although the polysulfide reaction was not. The mole ratio of polysulfide to thiosulfate formed by complete oxidation of the hydrosulfide was relatively independent of temperature. Oxidation below 60°C precipitated small quantities of amorphous sulfur droplets from the liquor. These

droplets upon aging crystallized to rhombic sulfur which in turn decomposed and re-dissolved in the black liquor.

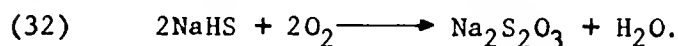
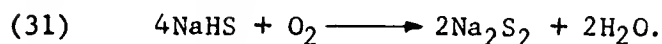
The method of contact affected the rate of reaction but not the quality nor quantity of the major inorganic reaction products. Oxidation at 60°C required the least volume of oxygen, but oxidation proceeded most rapidly at 75°C. Therefore, the optimum oxidation temperature was somewhere between 60°C and 75°C. When adequate gas-liquid contact was made available, the reaction rate was limited by the oxidation rate of hydrous sulfide. This oxidation very closely approximated a first-order reaction.

Evidence collected suggested that soluble material present in the black liquor catalyzed the oxidation of the hydrosulfide. Oxidation took place in two distinct steps: first, absorption of oxygen and, second, the utilization of this oxygen to oxidize the hydrous sulfide. Undesirable side reactions that apparently also utilize some of the absorbed oxygen were increasingly prevalent at temperatures above 60°C.

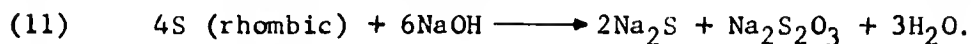
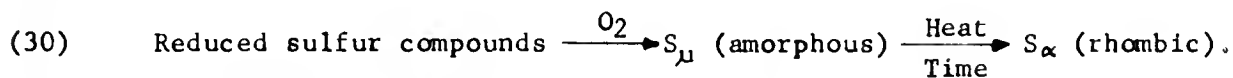
Pure oxygen had only limited effectiveness in oxidizing the odorous constituents of black liquor. Oxidation fixed the inorganic hydrous sulfide in the black liquor but at least a portion of the organics still remained volatile. These materials were subject to loss when the black liquor was recycled to reclaim the unused chemicals. The organic odors emitted from oxidized black liquor were identified and effective means to destroy the odors with ozone were studied. Approximate costs and suggestions for mill-scale application of pure oxygen and ozone were discussed.

On the basis of the previously described study of the oxidation of Kraft black liquor, the following conclusions were drawn:

1. The primary inorganic reactions that occurred during black liquor oxidation, at atmospheric pressure between 60°C and 89°C, were the conversion of sodium hydrosulfide to sodium polysulfide and sodium thiosulfate. The polysulfide and thiosulfate formed accounted for all of the oxidized hydrosulfide with an average experimental error of 3.9 per cent. In no instance was any sulfite or sulfate produced by oxidation. Equations 31 and 32 represent the predominant inorganic reactions.



2. Oxidation at temperatures of 60°C and below was conducive to sulfur formation. The sulfur precipitate, which averaged 4 to 5 milligrams per liter was in the form of tiny insoluble amorphous droplets. These droplets ranged in size from about 0.5 to 1.0 microns and crystallized to rhombic sulfur under the proper conditions. This crystallization required about three days at 25°C; the same effect was achieved in less time at elevated temperatures. Equations 30 and 11 represent the formation, crystallization, and eventual decomposition of the sulfur in black liquor.



Reactions 30 and 11 occurred in relatively small concentrations compared to the concentrations involved in reactions 31 and 32.

3. Temperature variation from 60°C to 89°C had little or no affect on the products of oxidation. Over this temperature range an average of 1.6 moles of sodium thiosulfate was produced for every one mole of disodium disulfide produced.

4. The method of contact affected the rate of oxidation but not the quality or quantity of the major inorganic reaction products.

5. Of the reactions 31 and 32, the latter was reversible although the former was not. Hydrosulfide was regenerated under anaerobic conditions by reversion of some of the thiosulfate. Maximum regeneration occurred when liquor was only 20 per cent to 40 per cent oxidized. A completely oxidized liquor regenerated less than 10 per cent of the initial sulfide content when stored for 12 hours. Therefore, the practice of storing the oxidized liquor before evaporation is unwise and should be discouraged.

6. Temperature had little effect on the reaction rate. Of the three temperatures tested, 75°C showed a slightly higher rate of oxidation. Area-time contact considerations were of prime importance and could control black liquor oxidation. When adequate gas-liquid contact was available, the chemical reaction, which was nearly a first-order reaction, determined the oxidation rate.

7. Oxidation at 75°C , using oxygen enriched with 1450 parts per million of ozone, did not increase the reaction rate of dissolved hydrosulfide. However, the mercaptan odor of the black liquor was eliminated. It was concluded, therefore, that ozone could be more effectively used to oxidize gaseous odors than black liquor.

8. The total oxygen consumed by the black liquor increased sharply with increased temperature. The oxygen consumption at 89°C was almost twice the consumption at 60°C with little over-all change in the hydrosulfide reaction rate. At the higher temperatures no changes in reaction products were noted; the greater oxygen consumption, indicated an increase in other side reactions which were probably organic. From the standpoint of minimizing oxygen consumption 60°C was the most desirable temperature at which to oxidize black liquor.

9. The observed time lag between oxygen absorption and utilization indicated that some oxygen transfer mechanism was involved in the oxidation process. Since a synthetic inorganic liquor containing hydrosulfide oxidized at a slower rate than black liquor, it was concluded that the organic materials in the black liquor catalyzed the oxidation of sodium hydrosulfide.

10. Oxidation stabilized the inorganic sulfur compounds in black liquor but had a limited influence on the odorous organic compounds. Pure oxygen failed to oxidize all of the volatile organic sulfur compounds; which could be stripped from the black liquor during or after oxidation. Methyl mercaptan, ethyl mercaptan, and methyl sulfide, but no hydrogen sulfide, were identified in the oxidation exhaust gases from this particular black liquor.

11. It was found that the oxidation exhaust gases could be deodorized effectively with 100 to 150 parts per million (at 25°C) of ozone. On the basis of this observation, it is suggested that the non-condensable gases from the evaporators and digesters be similarly deodorized with ozone. Ozone can be produced electrically for about

\$0.19 per pound where the power cost is \$0.02 per kilowatt-hour. At this cost 150 parts per million of ozone can be produced in an air stream at 25°C for about \$0.0035 per 1000 cubic feet.

12. To be feasible on a large scale, oxidation of black liquor with oxygen should be conducted in a closed system at about 60°C. Such a system must economically utilize all the oxygen supplied. Assuming no gas losses and an oxygen cost of \$0.09 per pound, oxidation will cost about \$1.17 per 1000 gallons of liquor treated.

CHAPTER VIII

SUGGESTIONS FOR FURTHER STUDY

In black liquor oxidation and related fields several areas require further investigation. Certain basic questions remain to be answered about the catalytic mechanisms of oxidation. Research and development will be necessary before a pure-oxygen system can be built and operated on a mill scale. If equipment can be built to oxidize the black liquor effectively using the minimum stoichiometric quantities of oxygen, a "Pure-Ox" system may prove economically feasible.

Research in the area of paper mill odor control using oxidation, chlorination, and catalytic oxidation remains virtually untouched. Much work needs to be accomplished in these fields before such methods can be applied to air-borne effluents.

In summarizing some of the research needed in the field of black liquor oxidation and odor control, it is suggested that information be gathered on the following:

1. Catalytic mechanisms involved in black liquor oxidation, including the effect of the addition of various catalysts on the rate of oxidation.

2. Effect of the addition of various inorganic substances such as NaOH, S, and Na₂S on oxidation rate.

3. The effect of pH control and any other possible methods of accelerating oxidation.

4. Formation and significance of trace compounds such as persulfates, hyposulfites and dithionates in black liquor as well as determining the exact composition of the sodium polysulfide.

5. Research and development on a "Pure-Ox" oxidation system with a closed, static oxygen flow and dynamic liquor flow and investigation of the utilization of oxygen under pressure.

6. Chemical reactions that take place when exhaust gases are treated with the ozone oxygen mixture and methods of improving mercaptan stabilization.

7. Application of catalytic combustion and chemical oxidation to deodorization of gaseous pulp mill effluents.

APPENDICES

APPENDIX I

METHODS OF CHEMICAL ANALYSIS

Method

Sodium sulfide in black liquor.

Reagents

Base electrolyte - 0.8 grams $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; 20 milliliters concentrated HCl; 50 milliliters 10 per cent Roccal (alkyl dimethyl benzyl ammonium chloride) diluted to 1 liter with distilled water.

p-Phenylenediamine dihydrochloride solution - 2.5 grams dye; 10 milliliters concentrated HCl diluted to 250 milliliters with distilled water. This solution is stable for 2 to 3 weeks.

Hydrogen sulfide gas.

Oxygen-free sodium hydroxide (0.2N).

Starch solution (2 to 3 grams per liter).

Standard sodium thiosulfate solution 0.025N - 6.205 grams of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ diluted to 1 liter with boiled distilled water. Thiosulfate is standardized against a known solution of potassium dichromate.

Standard iodine solution 0.025N - 10 grams of KI and 3.173 grams of I diluted to 1 liter with boiled distilled water. The iodine is standardized against the 0.025N sodium thiosulfate.

Procedure

1. To 48 milliliters of base electrolyte in a stoppered Nessler tube, a 0.15 milliliter sample of black liquor is added from a syringe by discharging the needle below the surface of electrolyte.
2. Swirl the tube gently to mix.
3. Let sample stand for 1 to 2 minutes.
4. Quickly add 2 milliliters of p-phenylenediamine dye, stopper and mix.
5. Allow color to form for more than 10 but less than 15 minutes.
6. Transfer the sample to a 500 milliliter graduated cylinder and dilute appropriately with distilled water.
7. Measure the optical density at 600 millimicrons against a similarly prepared and diluted blank.
8. Determine the sulfide from a previously prepared standard curve and express as grams per liter sodium sulfide.

Preparation of Standard Curve

1. Prepare a standard sulfide solution by injecting 100 cubic centimeters of H_2S into 50 milliliters of 0.2N NaOH in a sealed volumetric flask.
2. Add an aliquot of v milliliters of sulfide solution to an Erlenmeyer flask containing 25 milliliters of 0.025N iodine, 25 milliliters of 0.1N HCl, and 100 milliliters of boiled distilled water.
3. Titrate excess iodine with 0.025N sodium thiosulfate to a starch end point. Calculate the sulfide concentration as follows:
Grams per liter $\text{Na}_2\text{S} = (25.00 - \text{ml Na}_2\text{S}_2\text{O}_3) \times 0.025 \times 39 \times 1/v$.

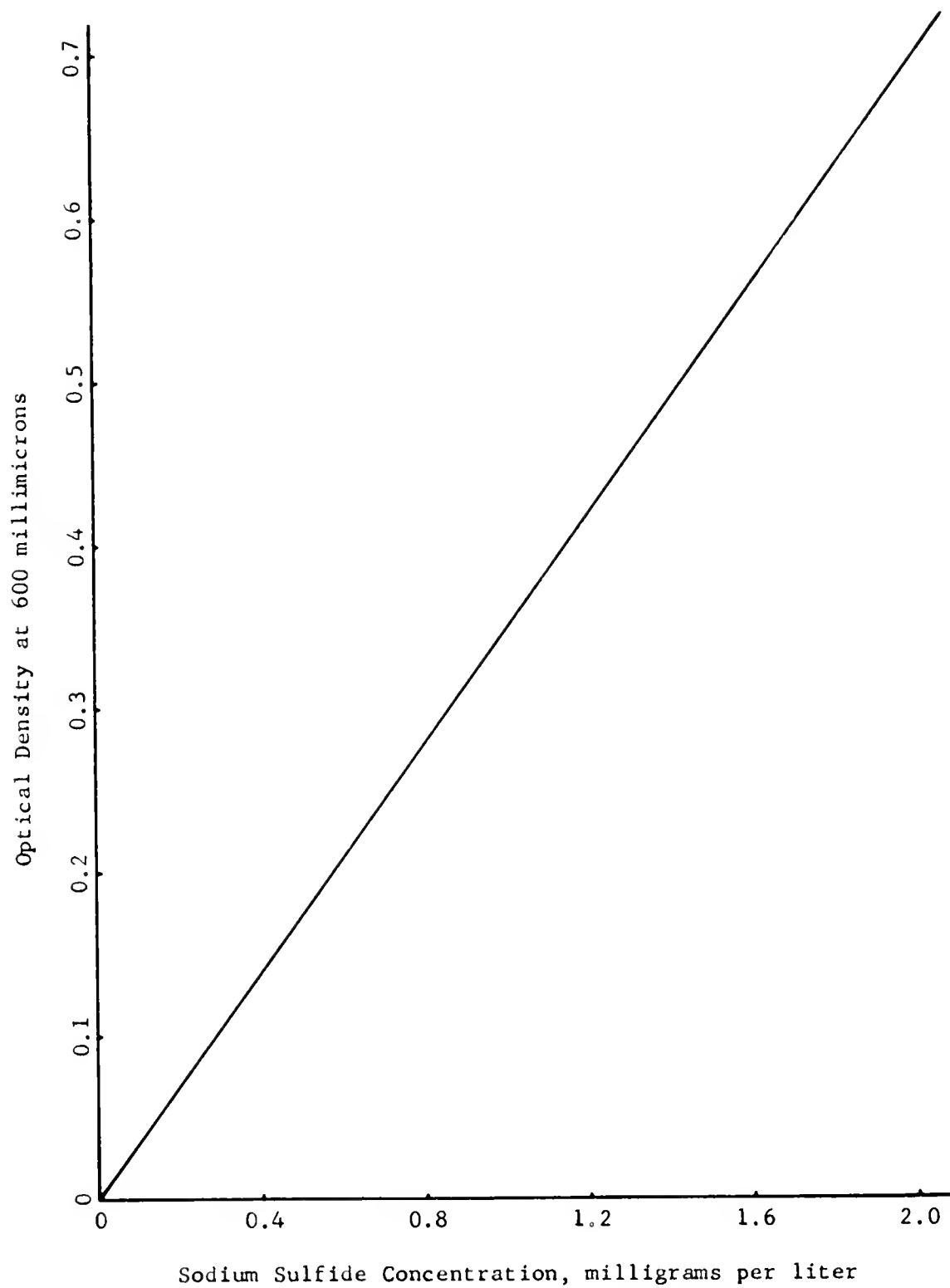


Fig. 18.-Sample standard curve for sodium sulfide analysis.

4. Add 0.15 milliliters of standard sulfide solution to 48 milliliters of base electrolyte and form color as described in steps 2 through 5 of the procedure.

5. Dilute standard and appropriate blank in two 500 milliliter graduated cylinders. The optical density at 600 millimicrons is measured for 4 or 5 dilutions. Beers' law holds for concentrations up to 3 milligrams per liter.

6. Plot curve of optical density vs. concentration.

Calculations

$$\text{Grams per liter Na}_2\text{S} = \frac{C \times \text{D.F.}}{3.00} \times 1.17$$

where: C = concentration of unknown in milligrams per liter

$$\text{D.F.} = \frac{V}{50}, \text{ and } V = \text{final diluted volume.}$$

Reference

Strickland, J. D. H., and Risk, J. B. "Rapid Absorptiometric Determination of Sulfide in Sulfate Pulp Black Liquor," TAPPI, 40, pp. 91-94 (February, 1957).

* * * * *

Method

Sodium polysulfide in black liquor.

Reagents

Hydrochloric acid (1:1).

Ammonium hydroxide (1:1).

Zinc Chloride.

Procedure

1. Dilute a 25 milliliter sample of black liquor to about 250 milliliters with distilled water. Add 0.2 grams of ZnCl_2 to precipitate the sulfides.
2. Acidify to pH 4.0 using 1:1 HCl and let sample stand to coagulate and settle precipitated lignin.
3. Remove the precipitate by filtration and collect the filtrate in a 400 milliliter beaker.
4. Acidify filtrate to pH 1.0 with 1:1 HCl and digest it for 2 to 3 hours at 75°C .
5. Collect precipitated sulfur in sintered glass crucibles and wash several times with distilled water.
6. Dry the crucibles at 80°C for about four hours, cool and weigh.
7. Calculate the results as grams per liter disodium disulfide.

Calculations

$$\text{Grams per liter Na}_2\text{S}_2 = (\text{grams S}^\circ) \times 40 \times 1.719.$$

Reference

Furman, N. H., Ed. Scott's Standard Methods of Chemical Analysis. Vol. I and II, 5th Ed., New York: D. Van Nostrand, 1939.

* * * * *

Method

Sodium sulfite and sodium thiosulfate in black liquor.

Reagents

Glycerin.

Formaldehyde solution (40 per cent).

Acetic acid solution (1:9).

Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$).

Sodium carbonate solution (10 per cent Na_2CO_3).

Lead acetate test solution (0.2M).

Starch solution (2 to 3 grams per liter).

Standard potassium dichromate solution 0.025N - 1.226 grams of dried $\text{K}_2\text{Cr}_2\text{O}_7$ diluted to 1 liter with distilled water.

Standard sodium thiosulfate solution 0.025N - 6.205 grams of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ diluted to 1 liter with boiled distilled water. Thiosulfate is standardized against a 0.025N solution of potassium dichromate.

Standard iodine solution 0.025N - 10 grams of KI and 3.173 grams of I diluted to 1 liter with boiled distilled water. The iodine is standardized against the 0.025N sodium thiosulfate.

Procedure

1. Pipet 25 milliliters of black liquor into a 250 milliliter volumetric flask and add 15 milliliters of glycerin.

2. Precipitate the organic matter and sodium sulfide by adding a freshly prepared ZnCO_3 suspension (made from 5 grams of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and 25 milliliters of 10 per cent Na_2CO_3).

3. Fill flask $\frac{2}{3}$ full and shake. Let the precipitate settle.

4. Test a few drops of the supernatant for sulfide with lead acetate and add more ZnCO_3 if necessary. Dilute to mark and let settle.

5. Filter through a vacuum funnel into a dry flask.
6. Pipet two 25 milliliter portions of the filtrate into 500 milliliter Erlenmeyer flasks, each containing about 100 milliliters of distilled water and 100 grams of ice. Analyze the first flask for $\text{SO}_3^=$ and the second for $\text{S}_2\text{O}_3^=$.
7. Add 1 milliliter of starch solution to first flask and acidify with 5 milliliters of 1:9 acetic acid.
8. Titrate with 0.025N iodine through rubber diaphragm until blue color persists for 10 to 15 seconds. Denote this volume of iodine in milliliters as A.
9. Add 5 milliliters of 40 per cent formaldehyde to second flask, swirl to mix and add 1 milliliter of starch solution. Acidify with 5 milliliters of 1:9 acetic acid.
10. Titrate with 0.025N iodine until a blue color persists for 10 to 15 seconds. Denote this titration as B.
11. Calculate the results as grams per liter Na_2SO_3 and $\text{Na}_2\text{S}_2\text{O}_3$.

Calculations

Grams per liter $\text{Na}_2\text{SO}_3 = (A - B) \times 0.063 \times 400 \times 0.025$.

Grams per liter $\text{Na}_2\text{S}_2\text{O}_3 = B \times 0.158 \times 400 \times 0.025$.

Reference

Standards of the Technical Association of the Pulp and Paper Industry. Testing Methods, Recommended Practices, and Specifications, Method T625m-48, New York: TAPPI.

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Method

Sodium sulfate in black liquor.

Reagents

Hydrochloric acid (concentrated).

Nitric acid (concentrated).

Ammonium hydroxide (1:1).

Methyl orange indicator.

Barium chloride solution (10 per cent BaCl_2).

Procedure

1. Pipet 25 milliliters of black liquor into a 250 milliliter beaker containing 100 milliliters of distilled water.
2. Neutralize the sample by adding 5 milliliters of concentrated HCl. Filter and wash the organic matter thoroughly with hot distilled water, collecting filtrate in 400 milliliter beakers. Digest briefly at 75°C and refilter.
3. Boil the filtrate gently for 10 minutes and cool.
4. Adjust to methyl orange end point with NH_4OH and add 1 milliliter of concentrated HCl excess.
5. Dilute to about 250 milliliters and heat to boiling.
6. Add 15 milliliters of 10 per cent BaCl_2 solution dropwise to hot solution while stirring.
7. Add a few more drops of BaCl_2 after partial settling. If precipitation complete, maintain solution at 80 to 90°C for 10 to 15 minutes. Set aside and let cool and settle for 1 to 2 hours.

8. Filter through Whatman No. 42 and wash with acidified (HNO_3) hot water until no chlorides are present in wash.
9. Place the filter paper in a tared crucible; heat slowly to destroy the paper; then fire at 800°C ; cool; and weigh.
10. Express the results as grams per liter Na_2SO_4 .

Calculations

Grams per liter Na_2SO_4 = grams BaSO_4 x 0.6086 x 40.

Reference

Standards of the Technical Association of the Pulp and Paper Industry. Testing Methods, Recommended Practices, and Specifications, Method T625m-48, New York: TAPPI.

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Method

Ozone concentration in a stream of oxygen.

Reagents

Acetic acid solution (1:5).

Alkaline iodide solution - 10 grams of KI and 4 grams of NaOH diluted to 1 liter with boiled distilled water.

Potassium iodate stock solution - 0.1000 grams of KIO_3 diluted to 1 liter with boiled distilled water.

Potassium iodate standard solution (5 micrograms per milliliter) - 25 milliliters of stock KIO_3 solution diluted to 500 milliliters with boiled distilled water.

Procedure

1. Draw a known volume of O_3 containing oxygen through a midget impinger filled with 30 milliliters of alkaline iodide solution.
2. Place the sample, or an aliquot diluted to 30 milliliters with fresh alkaline KI, in a 50 milliliter Nessler tube. Add sufficient distilled water to bring volume up to 40 milliliters.
3. Add to each sample, just before measuring the absorption, 10 milliliters of 1:5 acetic acid.
4. Stopper, mix and read the absorption at 352 millimicrons with water as the zero reference.
5. Calculate the concentration of ozone in parts per million from knowledge of the volume of oxygen absorbed and a previously prepared standard curve.

Preparation of Standard Curve

1. Pipet 3, 6, 9, 12, and 15 milliliter aliquots of standard iodate solution in 50 milliliter Nessler tubes. Dilute up to 30 milliliters with fresh alkaline iodide solution and then add 10 milliliters of distilled water to each tube.
2. The characteristic yellow iodine color is formed and absorption measured as described in steps 3 and 4 of the procedure.
3. Plot curve of optical density vs. concentration.

Calculations

$$\text{Parts per million } O_3 = \frac{\text{micrograms } O_3 \times \text{D.F.}}{\text{liters of } O_2 \text{ absorbed}} \times 0.467.$$

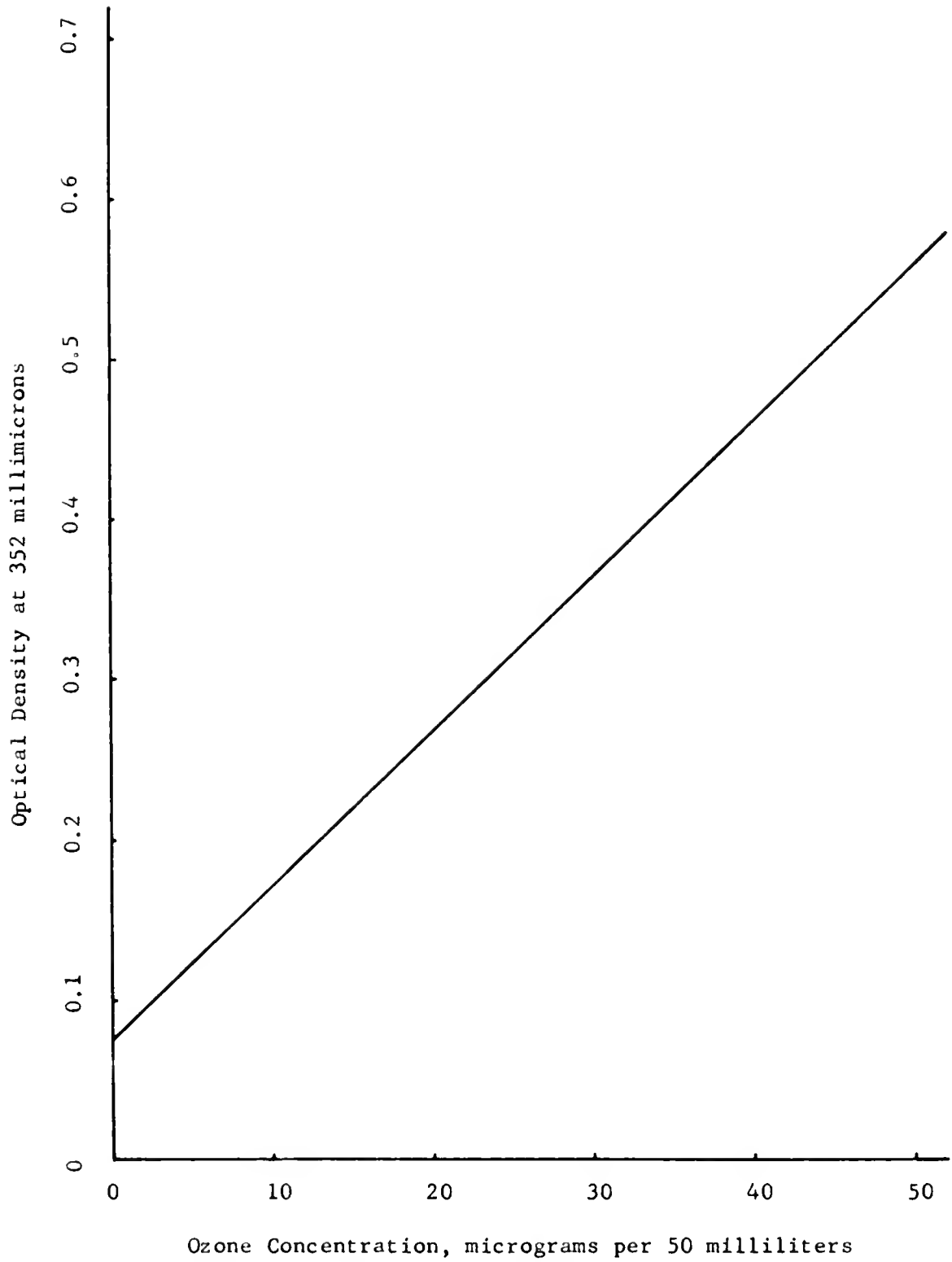


Fig. 19.-Sample standard curve for colorimetric ozone analysis.

Reference

Jacobs, M. B. The Chemical Analysis of Air Pollutants.

New York: Interscience, 1960.

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Method

Total solids, specific gravity, sulfated ash and organic matter in black liquor.

Reagents

Sulfuric acid (concentrated).

Procedure

1. Dry 25 milliliters of black liquor in a tared evaporating dish at 105°C for 24 hours; cool and weigh.
2. Express and calculate the total solids (oven dry) as grams per liter and percentage (by weight).
3. Ash the solids from the previous step to remove most of the organic matter.
4. Add a few drops of water and acidify to pH 4 with H₂SO₄.
5. Fire ash at 800°C to remove all organic matter, cool and weigh.
6. Assuming the residue left is pure Na₂SO₄, the sulfated or mineral ash is calculated and expressed as percentage of the total solids. The weight lost during firing is attributed to destruction of the organic matter.

Calculations

$$\text{Percentage total solids} = \frac{c - a}{b - a} \times 100$$

$$\text{Grams per liter total solids} = (c - a) \times 40$$

$$\text{Specific gravity} = \frac{(b - a)}{25 \text{ (S.G. of water)}}$$

$$\text{Percentage sulfated ash, as NaOH} = \frac{(d - a) \times 0.563}{(c - a)} \times 100$$

$$\text{Percentage organic matter} = 100 - \text{percentage SO}_4 = \text{ash}$$

where: a = tare weight of evaporating dish

b = tare + 25 milliliters black liquor

c = tare + 25 milliliters black liquor oven dry

d = tare + sulfated ash.

Reference

Standards of the Technical Association of the Pulp and Paper Industry. Testing Methods, Recommended Practices, and Specifications, Method T625m-48, New York: TAPPI.

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Method

Active alkali, caustic, and sulfidity in black liquor.

Reagents

Standard hydrochloric acid (0.50N). HCl is standardized against Na₂CO₃ to methyl orange end point.

Sodium carbonate (Na₂CO₃ anhydrous).

Methyl orange indicator.

Barium chloride solution (10 per cent BaCl₂).

Procedure

1. Pipet 50 milliliters of the black liquor into a 250 milliliter volumetric flask containing 100 to 150 milliliters of boiled distilled water.
2. Add 50 milliliters of 10 per cent BaCl_2 solution and dilute sample to 250 milliliters.
3. Allow to settle for 15 to 20 minutes and pipet 50 milliliter aliquot of the supernatant into a beaker containing distilled water.
4. Titrate potentiometrically with 0.50N HCl to a pH of 8.3.
5. Calculate the active alkali ($\text{NaOH} + \text{Na}_2\text{S}$), caustic, and percentage sulfidity using titrated value and the previously determined sulfide analysis.

Calculations

Grams per liter active alkali as $\text{Na}_2\text{O} = (\text{ml } 0.5\text{N HCl}) \times 0.0155$
 $\times 100 + (\text{gm/l } \text{Na}_2\text{S}) \times 0.397.$

Grams per liter caustic as $\text{NaOH} = (\text{ml } 0.5\text{N HCl}) \times 0.0155 \times 100$
 $- (\text{gm/l } \text{Na}_2\text{S}) \times 0.513.$

Percentage sulfidity = $\frac{(\text{gm/l } \text{Na}_2\text{S}) \times 0.397}{(\text{gm/l active alkali as } \text{Na}_2\text{O})} \times 100.$

Reference

Standards of the Technical Association of the Pulp and Paper Industry. Testing Methods, Recommended Practices, and Specifications, Method T625m-48, New York: TAPPI.

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Method

Total alkali and sodium carbonate in black liquor.

Reagents

Standard hydrochloric acid (0.50N). HCl is standardized against Na_2CO_3 to methyl orange end point.

Sodium carbonate (Na_2CO_3 anhydrous).

Methyl orange indicator.

Furfural.

Procedure

1. Pipet 25 milliliters of the black liquor into a 500 milliliter volumetric flask containing 100 to 150 milliliters of boiled distilled water.

2. Add 10 milliliters of furfural, mix, and dilute sample to 500 milliliters.

3. Titrate the sample potentiometrically with 0.50N HCl to a pH of 4.6.

4. Calculate the total alkali ($\text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 + 1/2 \text{Na}_2\text{SO}_4$) and express as grams per liter of Na_2O . Determine sodium carbonate by subtraction of known alkalies from this total.

Calculations

Grams per liter total alkali as $\text{Na}_2\text{O} = (\text{ml } 0.50\text{N HCl}) \times 0.0155$
 $\times 400.$

Grams per liter sodium carbonate as $\text{Na}_2\text{O} = \text{total alkali (gm/l as } \text{Na}_2\text{O)} - \text{active alkali (gm/l as } \text{Na}_2\text{O)} - 1/2 \text{ sodium sulfate}$
 $\times 0.436.$

Grams per liter sodium carbonate as $\text{Na}_2\text{CO}_3 = \text{Na}_2\text{CO}_3$ (gm/l as Na_2O) x 1.71.

Reference

Casey, J. P. Pulp and Paper. Vol. I, New York: Interscience, 1952.

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Method

Hydrogen sulfide in exhaust gases.

Reagents

N, N-Dimethyl-p-phenylenediamine sulfate sulfuric acid solution - 2.5 grams of high purity N, N-Dimethyl-p-phenylenediamine dye diluted to 1 liter with 1:1 sulfuric acid solution. This solution is stable for two months.

Sulfuric acid solution (1:1).

Ferric chloride solution - 100 grams $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ diluted to 100 milliliters with distilled water.

Hydrogen sulfide gas.

Oxygen free sodium hydroxide (0.2N).

Starch solution (2 to 3 grams per liter).

Standard sodium thiosulfate solution 0.025N - 6.205 grams of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ diluted to 1 liter with boiled distilled water. Thiosulfate is standardized against a known solution of potassium dichromate.

Standard iodine solution 0.025N - 10 grams of KI and 3.173 grams of I diluted to 1 liter with boiled distilled water. The iodine is standardized against the 0.025N sodium thiosulfate.

Zinc acetate scrubbing solution (2 per cent) - 20 grams

$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$; 3 drops of glacial acetic acid diluted to 1 liter with distilled water.

Glacial acetic acid.

Procedure

1. Pass the exhaust helium stream from gas chromatograph through a fritted gas absorber containing 100 milliliters of 2 per cent zinc acetate solution to absorb the H_2S .
2. Add 200 milliliters of boiled distilled water to a 250 milliliter volumetric flask.
3. Add 5 milliliters of N, N-Dimethyl-p-phenylenediamine sulfate sulfuric acid solution to the flask and mix.
4. Add sample aliquot of v milliliters of zinc acetate containing from 10 to 300 micrograms of sulfide to the flask, and immediately stopper. Gently swirl.
5. Add 10 drops of ferric chloride solution to flask and mix.
6. Allow 10 minutes for blue color development. Then dilute to the 250 milliliter mark with distilled water and mix. Allow 15 additional minutes for full color development.
7. Measure the optical density at 670 millimicrons against a similarly prepared blank.
8. Determine the sulfide from a previously prepared standard curve and express as total grams of H_2S absorbed.

Preparation of Standard Curve

1. Prepare a standard solution of sulfide by injecting 0.72 cubic centimeters of H_2S into 50 milliliters of 0.2N NaOH in a sealed volumetric flask.

2. Add a 15 milliliter aliquot of standard sulfide solution to an Erlenmeyer flask containing 25 milliliters of 0.025N iodine, 25 milliliters of 0.1N HCl, and 100 milliliters of boiled distilled water.

3. Titrate excess iodine with 0.025N sodium thiosulfate to a starch end point. Calculate the sulfide concentration as follows:

$$\text{Grams per liter } \text{S}^= = (25.00 - \text{ml Na}_2\text{S}_2\text{O}_3) \times 0.025 \times 16 \times 1/15.$$

4. Add 2, 5, 10, and 15 milliliter aliquots of standard sulfide solution to flasks containing 200 milliliters of boiled distilled water. Form color as described in steps 2 through 5 of the procedure. The optical densities of the standards are measured at 670 millimicrons against a similarly prepared blank.

5. Plot curve of optical density vs. concentration.

Calculations

$$\text{Grams of } \text{H}_2\text{S} = \mu\text{gm } \text{S}^= \times \text{D.F.} \times 1.062 \times 10^6.$$

where: D.F. = $100/v$, and

v = aliquot in milliliters.

Reference

Hendrickson, E. R., et al. Atmospheric Pollution Technical Bulletin No. 11. National Council for Stream Improvement, New York, 1959.

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Method

Sulfur compounds in exhaust gas, analysis by gas chromatography.

Equipment

Sample collection.- The exhaust gases from black liquor oxidation first pass through a condenser held at 0°C in an ice water bath. Final dessication is achieved by next passing the gas through a column of calcium sulfate. By keeping the calcium sulfate at a temperature of 55°C , the remaining water vapor is removed from the exhaust, while the volatile sulfur compounds are not. Next the exhaust passes through a freeze-out trap containing 3 inches of 6-16 mesh silica gel and the sulfur compounds are condensed on the gel at -78.5°C . This temperature is achieved by submersing the trap in a Dewar flask containing a mixture of dry ice and methyl ethyl ketone. A detailed flow diagram of the sampling train is shown in Figure 7.

Chromatographic analysis.- After concentration in the silica gel trap the sample is desorbed at 100°C and passed through a custom built,⁴⁶ gas-liquid chromatograph. The chromatograph is equipped with a 1/4 inch x 8 foot, Triton X-100 adsorption column; a Gow-Mac T.E. III, thermal conductivity cell; and a Varian, type G-11A, 20 millivolt graphic recorder. The chromatograph uses helium as a carrier gas.

Procedure

1. Bring the oxidation chamber up to temperature and flush with oxygen.
2. Turn on the heating tapes around the exhaust line and maintain the gas above the dew point.

3. Connect sampling equipment to the exhaust line with Nalgene connectors and heat the drying tube furnace up to 55°C.
4. Set the water condenser in the flask containing the ice water mixture.
5. Set the silica gel freeze-out trap into the Dewar flask containing the dry ice, methyl ethyl ketone mixture.
6. With all connections in place, pour 1 liter of black liquor into the oxidizing chamber. Reseal the chamber, start the stirrer, and set the oxygen flow at 450 cubic centimeters per minute. Note the initial time and gas meter reading.
7. Analyze the black liquor for sulfide every 15 minutes and when no more than 0.05 grams per liter of Na_2S remains, stop the stirrer, and turn off the oxygen. Note the final time and the gas meter reading.
8. Remove the freeze-out trap from the exhaust line and connect to the gas chromatograph. Place a fritted, gas absorption bottle containing 100 milliliters of 2 per cent zinc acetate solution on the exhaust line of the chromatograph.
9. Set the helium pressure at 5.0 pounds per square inch and maintain the Triton X-100 column and all the tubing at 100°C. Maintain a current of 150 milliamperes through the thermal conductivity cell during analysis.
10. Remove the flask containing the dry ice methyl ethyl ketone mixture and rapidly heat the silica gel trap to 100°C.
11. Remove the zinc acetate scrubber from the chromatograph exhaust after the hydrogen sulfide is completely elutriated (approximately 6 minutes).

12. Identify the odorous organic gases in the sample on the basis of their elutriation times (see Table 19).

13. Analyze for H_2S the contents of the zinc acetate absorber by the N, N-Dimethyl-p-phenylenediamine sulfate method. Express results as grams of H_2S .

14. Determine the sulfides and mercaptans present in the condensate from the ice water trap. Determine the sulfides colorimetrically using the p-Phenylenediamine dihydrochloride method. Determine the total sulfides and mercaptans present using a starch, 0.025N iodine titration. The difference between the colorimetric and titrimetric analysis indicates the amount of mercaptans present.

Calculations

Grams of H_2S in the sample = grams of H_2S + A (see calculations for methylene blue analysis).

Grams of H_2S in the condensate = A = $gm/l Na_2S \times 0.436 \times$ volume of condensate in liters (see calculations for p-Phenylenediamine dihydrochloride sulfide analysis).

Grams of $H_2S + HS^-$ in the condensate as H_2S = B = $0.025 \times 39 \times$ volume of iodine in liters \times volume of condensate in liters (see p-Phenylenediamine dihydrochloride sulfide analysis -- preparation of standard curve steps 2 and 3).

Grams of HS^- in the condensate as H_2S = B - A

Reference

Adams, D., et al. Atmospheric Pollution Technical Bulletins Nos. 5, 6, and 13. National Council for Stream Improvement, New York, 1958, 1959, and 1960.

TABLE 19

GAS CHROMATOGRAPHY INSTRUMENT CALIBRATION

Sensitivity 150 Milliamperes
Helium 5.0 Pounds per Square Inch
8 Foot Triton X-100 Column at 100°C

Gas	Retention Time in Minutes
Methyl Mercaptan CH_3SH	3.6
Hydrogen Sulfide H_2S	7.3
Ethyl Mercaptan $\text{C}_2\text{H}_5\text{SH}$	24.0
Methyl Sulfide $(\text{CH}_3)_2\text{S}$	31.0

APPENDIX II

DETERMINATION OF REACTION CONSTANTS

The reaction known as black liquor oxidation is composed of two finite processes: first, the mass transfer of an oxidizing gas through a gas-liquid interface and second, the utilization of the dissolved gas to oxidize the black liquor. Since the oxidation of the inorganic hydrosulfide in the black liquor is the prime reaction concerned, the kinetics can be expressed by the semi-empirical relationship:

$$(29) \quad \frac{dc}{dt} = K (C + bP)$$

This equation indicates that the instantaneous change in sulfide content depends jointly on the residual sodium sulfide concentration, C , and the oxygen partial pressure, P . K , is the overall reaction rate proportionality constant and b is the oxygen absorption rate proportionality constant. Product bP is indicative of the rate of oxygen absorption and the smaller this value is, the more closely the oxidation of sulfide approaches a first order reaction.

During any experimental test the volume of black liquor changed slightly as samples were taken for analysis, and also as a result of small imbalances in the evaporation-condensation rates at the black liquor surface. Since this change in volume was small it can be

neglected and equation 29 integrates to the form:

$$(34) \quad \frac{2.303}{K} \log (C + bP) = t$$

Thus a plot of $\log (C + bP)$ vs. t is a straight line with a slope of $\frac{2.303}{K}$. Equation 34 can be rearranged to obtain a direct expression for the velocity constant, K .

$$(35) \quad K = 2.303 \log (C + bP) / t.$$

The data from Figures 12 and 13 are plotted in Figures 20 and 21 and the values of K and b determined. Constant b is determined by successive approximations. A value is assumed and successively adjusted until the plot of $\log (C + bP)$ vs. t is a straight line. Once b is established K may be determined using equation 35.

The graphs of $\log (C + bP)$ vs. t for static and dynamic oxidation are presented in Figures 20 and 21 respectively.

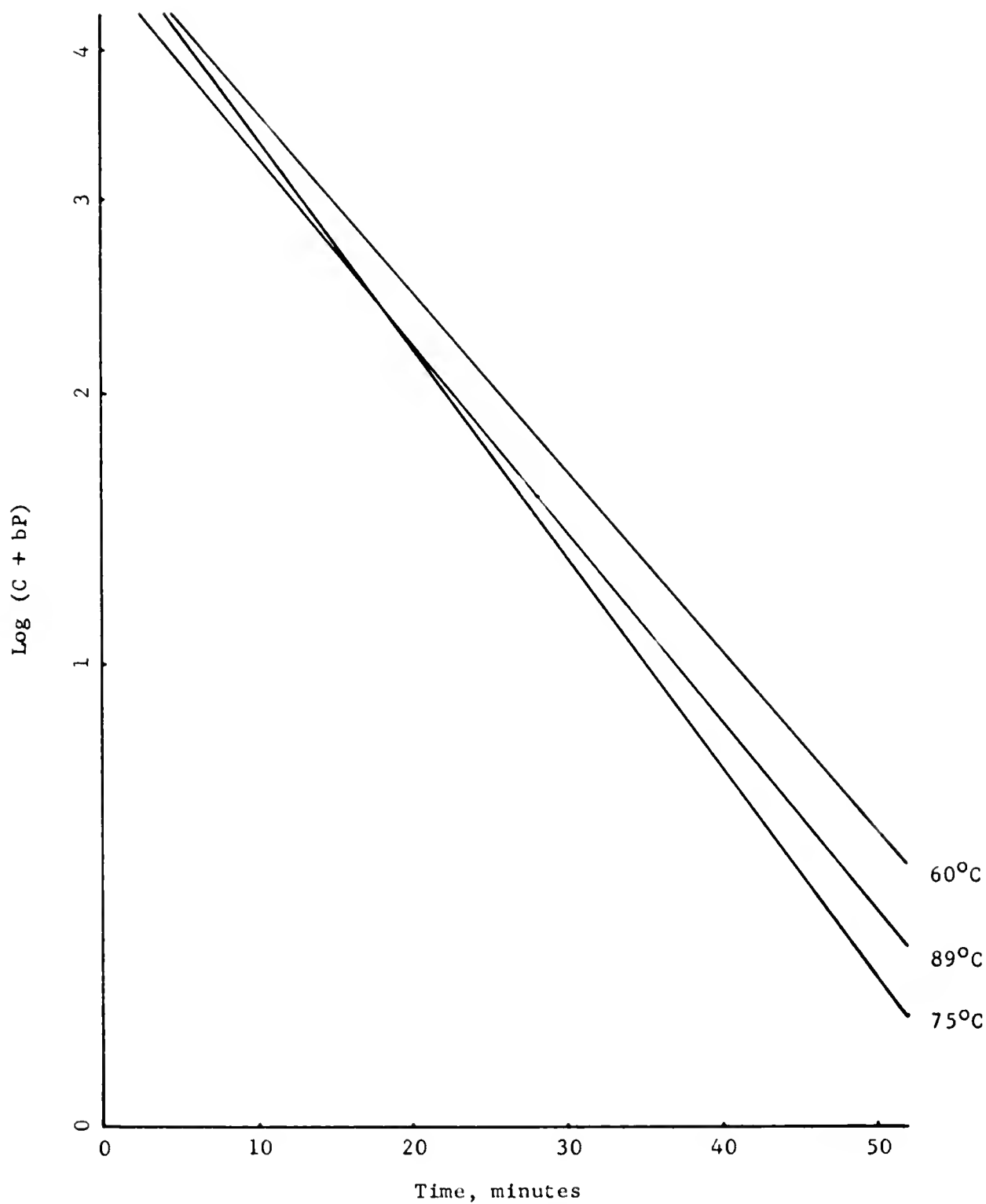


Fig. 20.-Curve fitting procedures for determining the oxidation kinetics of sodium sulfide in black liquor. System using static oxygen feed and temperatures of 60°C to 89°C.

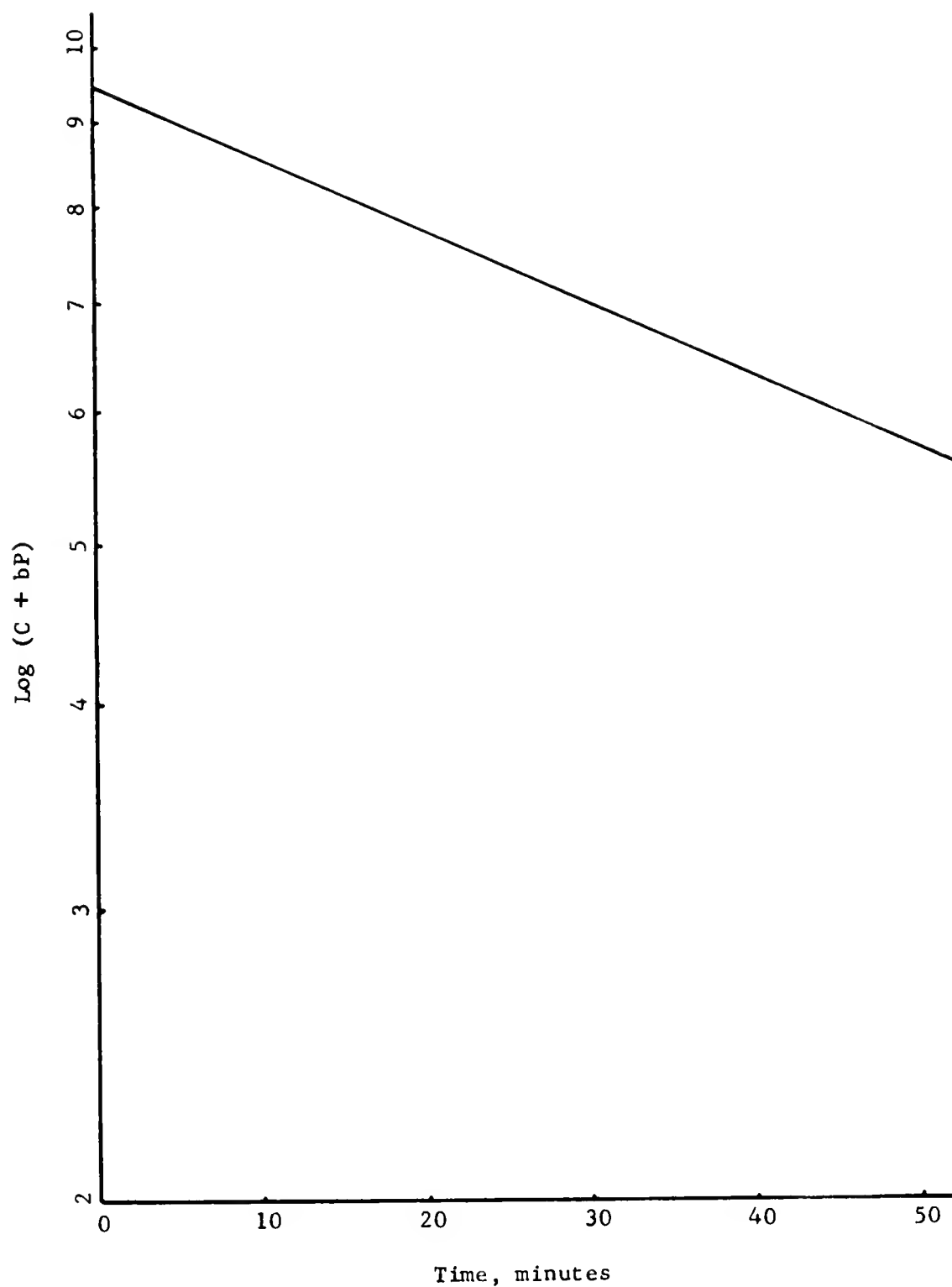


Fig. 21.-Curve fitting procedures for determining the oxidation kinetics of sodium sulfide in black liquor. System using dynamic oxygen feed at a temperature of 75°C.

APPENDIX III

COMPLETE BLACK LIQUOR ANALYSIS

Batch No. 1

Date Collected: March 3, 1961

Percentage total solids	= 14.84
Total solids, grams per liter	= 158.4
Specific gravity	= 1.071
Sulfated ash percentage as NaOH	= 31.4
Percentage organic matter	= 68.6
pH	= 11.80
NaOH, grams per liter	= 10.99
Active alkali, grams per liter as Na ₂ O	= 8.33
Percentage sulfidity	= 29.2
Na ₂ S, grams per liter	= 6.12
Na ₂ S ₂ O ₃ , grams per liter	= 5.29
Na ₂ SO ₃ , grams per liter	= 0.0
Na ₂ SO ₄ , grams per liter	= 3.28
Na ₂ CO ₃ , grams per liter as Na ₂ O	= 11.6

Batch No. 2

Date Collected: March 24, 1961

Percentage total solids	= 15.38
Total solids, grams per liter	= 165.5
Specific gravity	= 1.080
Sulfated ash percentage as NaOH	= 31.4
Percentage organic matter	= 68.6
pH	= 11.80
NaOH, grams per liter	= 11.22
Active alkali, grams per liter as Na_2O	= 8.81
Percentage sulfidity	= 27.2
Na_2S , grams per liter	= 6.05
$\text{Na}_2\text{S}_2\text{O}_3$, grams per liter	= 5.80
Na_2SO_3 , grams per liter	= 0.0
Na_2SO_4 , grams per liter	= 3.48
Na_2CO_3 , grams per liter as Na_2O	= 12.2

Batch No. 3

Date Collected: May 5, 1961

Percentage total solids	= 14.86
Total solids, grams per liter	= 158.5
Specific gravity	= 1.071
Sulfated ash percentage as NaOH	= 30.4
Percentage organic matter	= 69.6
pH	= 11.81
NaOH, grams per liter	= 11.20
Active alkali, grams per liter as Na_2O	= 8.30
Percentage sulfidity	= 27.80
Na_2S , grams per liter	= 5.80
$\text{Na}_2\text{S}_2\text{O}_3$, grams per liter	= 5.55
Na_2SO_3 , grams per liter	= 0.0
Na_2SO_4 , grams per liter	= 3.60
Na_2CO_3 , grams per liter as Na_2O	= 11.8

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BIOGRAPHICAL SKETCH

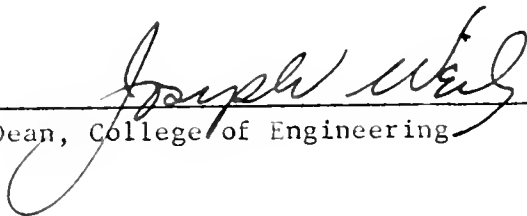
The author was born in Manhattan, New York, on April 23, 1936. Upon graduating with honors from Brooklyn Technical High School, he attended Cooper Union College in New York on a full tuition scholarship. He was awarded his bachelor's degree in Civil Engineering in June, 1957. Attending Graduate School at the University of Florida the author received the degree of Master of Science in Engineering in January, 1959. Since that time he has conducted additional graduate studies at the University of Florida.

The author has worked for a consulting engineer, the Mead Paper Corporation, and the United States Public Health Service. He holds an Engineer-in-Training certificate from New York State and is an Associate Member of the American Society of Civil Engineers.

Mr. Ricca is single and his immediate family is his mother and sister.


This dissertation was prepared under the direction of the Chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Engineering and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

February 3, 1962

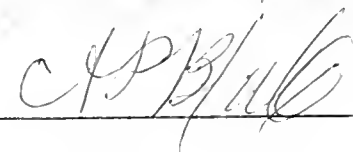

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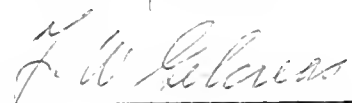
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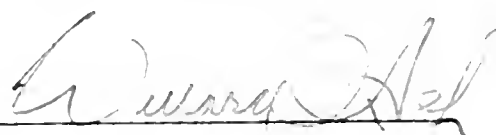
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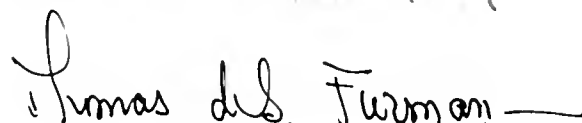

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